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# Canadian Journal of Research

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VOL. 14, SEC. A.

FEBRUARY, 1936

NUMBER 2

## MAGNETIC EFFECTS AND CURRENT SENSITIVITY OF SUPERCONDUCTING FILMS<sup>1</sup>

BY A. D. MISENER<sup>2</sup>

### Abstract

The work described in this paper is a continuation of the investigation of the anomalous behavior of superconducting metals in the form of thin films (12, 2–0.3 $\mu$ ). The manner in which an external magnetic field will penetrate when applied to superconducting films of various thicknesses at a variety of temperatures below their transition points has been studied. It is found that there is a critical field that will penetrate the film, and that this field is less than the threshold field required to restore the resistance of the film at the same temperature. Even for fields much larger than the threshold field, the films act as partial magnetic shields and diminish the field strength by an almost constant amount.

By measuring the current required to restore the resistance of films formed on cylindrical supports of different diameters, it is shown that their current sensitivity is due to a surface density of current. The critical magnetic field associated with this threshold current is less than either the threshold field (external) or the critical field for penetration. The similarity between these effects and those found for certain superconducting alloys is discussed.

### I. Introduction

The investigation of the superconductivity of thin metallic films (2, 8, 9) has shown that in several respects they behave in a manner analogous to that of certain of the superconducting alloys. The external magnetic field required to restore the resistance of thin films of tin is very much greater than that required for "massive" samples of the metal. This corresponds to the large threshold fields found for superconducting alloys (1). Silsbee's hypothesis regarding the maximum current that can be carried by a superconductor (12), while verified for pure metals in massive samples (10), is valid neither for certain alloys (4) nor for thin films of pure metals.

This similarity of behavior has led to the further investigation of the superconductivity of thin films along lines suggested by other "abnormalities" in the behavior of superconducting alloys.\* Results reported by de Haas and Casimir-Jonker (3) as well as those of Rjabinin and Schubnikow (11) show that an external magnetic field will penetrate certain alloys at a field strength far below that required to restore their resistance.

<sup>1</sup> Manuscript received January 2, 1936.  
Contribution from the McLennan Laboratory, Department of Physics, University of Toronto, Toronto, Canada.

<sup>2</sup> Holder of a bursary under the National Research Council of Canada.

\* For a discussion of normal and anomalous superconductors see H. Grayson Smith and J. O. Wilhelm, *Reviews of Modern Physics*, Vol. 7, No. 4, 1935.

The latter authors also studied the question of the maximum current strength, and found that the direct sensitivity to current, apart from the magnetic field produced, does not indicate a maximum current density throughout the wire, but rather a maximum surface density of current. Consequently, the investigations with thin films of tin reported herewith were undertaken: (i) to find, by means of exploring coils placed inside cylindrical films, the manner in which an external field would penetrate the film; (ii) to determine the maximum current which would be carried by cylindrical films of the same thickness on supports of different diameters, and thus determine the basis of their sensitivity to current.

## II. Penetration of Magnetic Field

### (1) Preparation of Films

Thin films of tin were deposited electrolytically on the outer surface of German silver tubes (outer diameter = 0.471 cm., wall thickness = 0.005 cm.). The method employed was similar to that described previously (2). The plating anode was a cylinder of commercial "pure tin" 6 cm. in diameter and 14 cm. long; the ends were left open to allow free circulation of the plating

solution which was kept well stirred. A length of the German silver tubing was used as cathode, its ends being closed so that the outer surface only would come in contact with the plating solution; it was connected to the negative terminal of the accumulator, and supported coaxially inside the tin anode. Sufficient potential difference was maintained to provide a plating current of approximately 0.2 amp. per square decimeter of the cathode area. The plating solution or "bath" used was one described by Mathers and Bell (5); the addition agent was resin.

To prepare the tubes for successful plating they had to be thoroughly cleaned. They were washed first in absolute alcohol, then in hydrochloric acid and finally in boiling distilled water, dried and weighed. After plating they were washed in boiling distilled water, dried and re-weighed. From the

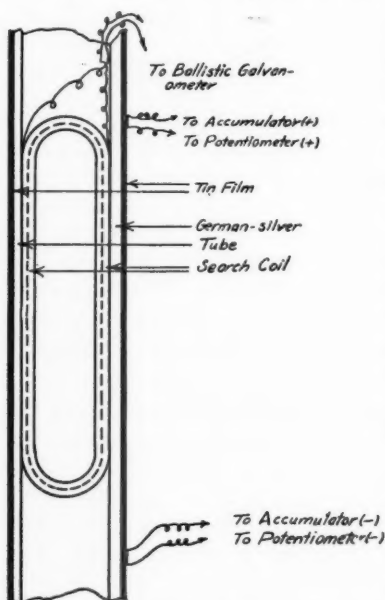


FIG. 1. Experimental arrangement for measuring the penetration of external magnetic fields through superconducting films of tin.

increase in weight the average thickness of the film deposited was calculated. A coating of glyptal lacquer was then applied to the films to protect them during subsequent handling; this covering of glyptal lacquer has no effect on the superconductive properties of the film (2).

Samples, 3 to 4 cm. in length, were cut from the central portions of the plated tubes and current and potential leads attached to the tin films with solder of low melting point. Exploring coils of fine copper wire (approximately 70 turns) were wound on hard rubber formers and placed inside the tubes. The arrangement is illustrated in Fig. 1. Three tubes with their exploring coils were mounted in the cryostat, which was placed between the poles of a large electromagnet. As any one tube was at least 3 cm. from its neighbors, the distortion of the magnetic field caused by the one becoming superconducting (6, 7) would be negligible in the vicinity of the others. The resistance of the various tin films was measured by the usual potentiometer method, a constant current of 5 ma. being used. The exploring coils were connected to a sensitive ballistic galvanometer.

## (2) Method

The following method of procedure was observed:

(a) At 4.2° K. various field strengths were applied transversely to the films, the ballistic throw of the galvanometer being read on both the make and break of the current through the electromagnet.

(b) The temperature of the liquid helium bath was then lowered, and the transition curve of the film obtained by measuring its resistance with the potentiometer while the bath was cooling.

(c) Some definite temperature below the transition temperature of the film was chosen, and the temperature of the bath kept constant at that value. Another set of readings of the ballistic throw produced by making and breaking fields of known strength was taken.

(d) At the same time the potentiometer was used to measure the resistance restored in the film by the external field.

(e) Procedures (c) and (d) were repeated at lower temperatures until the amount of the helium in the cryostat was not sufficient to keep the temperature constant over the entire length of the samples.

(f) The temperature of the bath was raised to that of liquid helium boiling under atmospheric pressure (4.2° K.), and as the samples gradually warmed up above their superconducting transition points the readings (a) were repeated.

Since German silver is an alloy of copper (55%), zinc (25%) and nickel (20%), it might be expected to show peculiar magnetic properties at very low temperatures. These might arise either from its ferromagnetic component or from the fact that it is an alloy with one superconducting component (Zn). Consequently a determination of the penetration of external magnetic fields into a blank tube with no tin coating was made at 4.2° K. and 2.5° K. The results are shown in Fig. 2, from which it is seen that over the range of temperature employed in this investigation there is no difference in penetration caused by the German silver tubes used as supports for the films. There was no change in the resistance of the sample tube ( $0.01060 \omega$ ) when it was cooled from 4.2° K. to 2.5° K. and therefore it is deduced that German silver is not a superconductor above 2.5° K.

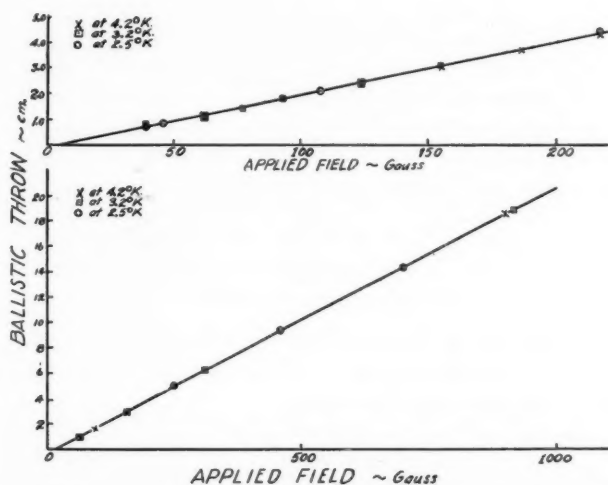


FIG. 2. Penetration of external magnetic field through the German silver tubes used as support for the tin films.

### (3) Results

The relation between the applied field,  $H$ , and the magnetic induction inside the film showed the same characteristics for all the films studied. These are illustrated by the typical graphs, Fig. 3 and 4, which show the penetration of a transverse magnetic field through a tin film of thickness  $1.6 \mu$  at temperatures  $0.5^\circ$  and  $1.10^\circ$  below its superconducting transition point ( $3.72^\circ$  K.). The broken curve shows the manner in which the resistance of the film was restored by the external magnetic field. The results obtained with films of different thickness and at various temperature differences ( $\Delta T$ ) below their normal transition points are shown in the following tables.

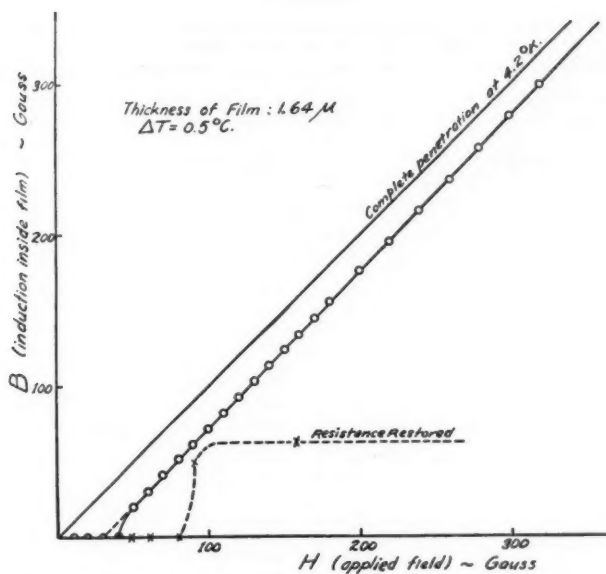


FIG. 3. Penetration of external magnetic field through tin film ( $1.6 \mu$ ) at a temperature of  $0.5^\circ$  below its transition point.

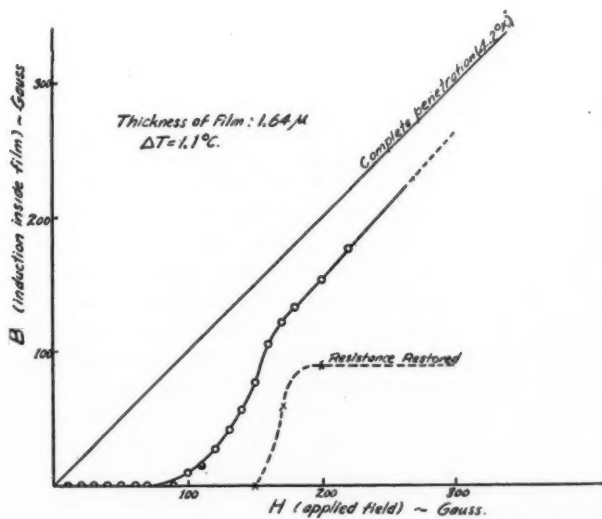


FIG. 4. Penetration of external magnetic field through tin film ( $1.6 \mu$ ) at a temperature of  $1.1^\circ$  below its transition point.

TABLE I

PENETRATION OF EXTERNAL MAGNETIC FIELD INTO TIN FILMS AT VARIOUS TEMPERATURES  
BELOW THEIR TRANSITION POINTS

Film thickness, 12.2 $\mu$					Film thickness, 3.10 $\mu$				
<i>H</i> Applied field, gauss	<i>B</i> Induction inside film				<i>H</i> Applied field, gauss	<i>B</i> Induction inside film			
	$\Delta T =$ 0.40°	0.70°	1.00°	1.90°		$\Delta T =$ 0.40°	0.70°	1.00°	1.90°
10	0	0	0	0	10	0	0	0	0
20	0	0	0	0	20	0	0	0	0
30	0	0	0	0	30	2	0	0	0
40	15	0	0	0	40	17	0	0	0
50	26	0	0	0	50	29	16	0	0
60	37	0	0	0	60	41	27	5	0
70	48	11	0	0	70	53	39	17	0
80	60 ( <i>R</i> )	26	0	0	80	65	50	30	10
90	70	38	0	0	90	76	60	45	24
100	80	49	5	0	100	87 ( <i>R</i> )	71	56	33
110	92	61	20	0	110	100	82	66	44
120	103	72	34	0	120		94	77	56
130		83	48	10	130		105	87	68
140		94	60	21	140		116	98	80
150		105	72	36	150		127	109	91
160		116 ( <i>R</i> )	85	49	160		138	120	103
170		127	96	62	170		148 ( <i>R</i> )	130	115
180		138	109	76	180		160	141	126
190		149	120	87	190		170	152	137
200		160	132	99	200		182	163 ( <i>R</i> )	149
220		185	155 ( <i>R</i> )	124	220		205	183	174
240		208	178	148	240			205	198
260			200	168	260			226	219
280			225	190	280				241
300				215	300				265
320				236 ( <i>R</i> )	320				288
340				260	340				312 ( <i>R</i> )
360				281	360				335

Throughout the tables the letter *R* indicates the value of the external field at which the ordinary electrical resistance of the sample is restored. Contrary to what might be expected, there is no apparent difference in the penetration of the field just before and after the electrical resistance has been restored. It is seen that for weak fields the tin films act as perfect magnetic shields. As the field strength is increased, a threshold value is reached at which penetration of the film begins. As the field strength is further increased, the amount penetrating the film is increased proportionally. It is remarkable that this relation holds at field strengths far beyond that required to restore the resistance of the film, the induction inside the film remaining less than the applied field by an amount approximately equal to the critical field strength.

As was anticipated, the value of this critical field varied for films of different thicknesses and was dependent upon the temperature to which

TABLE II  
PENETRATION OF EXTERNAL MAGNETIC FIELD INTO TIN FILMS AT VARIOUS TEMPERATURES  
BELOW THEIR TRANSITION POINTS

Film thickness, 1.64 $\mu$							Film thickness, 0.64 $\mu$		
<i>H</i> Applied field, gauss	<i>B</i> Induction inside film						<i>H</i> Applied field, gauss	<i>B</i> Induction inside film	
	$\Delta T = 0.40^\circ$	0.50°	0.70°	1.00°	1.1°	1.9°		$\Delta T = 0.30^\circ$	1.0°
10	0	0	0	0	0	0	10	0	0
20	0	0	0	0	0	0	20	0	0
30	0	0	0	0	0	0	30	0	0
40	18	0	0	0	0	0	40	34	20
50	28	20	0	0	0	0	50	54	31
60	38	31	0	0	0	0	60	66	42
70	48	42	18	0	0	0	70	77	52
80	58 (R)	52	30	0	0	0	80	87	63
90	68	62	40	24	0	0	90	97 (R)	74
100	78	72 (R)	50	37	10	2	100	106	85
110	88	82	60	52	15	10	120	126	105
120	98	93	71	65	27	20	140	144	126
130	107	103	82	75	41	50	160	160	147
140	118	113	93	85	56	78	200	200	190 (R)
150	128	124	104	95	77	92			
160	138	135	114 (R)	106	105	104			
170	148	145	123	117	121	116			
180	157	156	133	128	132	128			
200	177	176	155	151	153	146			
220		196	177	171 (R)	176 (R)	164			
240		216	198	192		184			
260		237		215		204			
280		258				225			
300		279				248			
320		300				268			
340						289			
360						310 (R)			

the film was cooled. It will be noticed that for all the films the value for the induction seems to be slowly approaching that for complete penetration. Consequently, for one of the films the investigation was carried to high field strengths. The results are shown in Table III, and it is seen that the shielding effect of the film persists at field strengths 20 times that required to restore the electrical resistance. In all the magnetic field measurements with the exploring coil, the limit of error is  $\pm 5$  gauss. Within this limit of error the values of the inductions on making and on breaking the current through the electromagnet were equal in all cases. Thus no field is "locked in" as was the case for alloys (3).

TABLE III  
PENETRATION OF STRONG  
EXTERNAL MAGNETIC FIELDS  
INTO A TIN FILM (1.64 $\mu$ )  
AT A TEMPERATURE OF  
0.5° BELOW ITS TRANS-  
ITION POINT

<i>H</i> Applied field, Gauss	Induction inside film $\Delta T = 0.50^\circ$
60	15
300	260
600	570
900	873
1200	1175
1500	1478
1800	1780
2100	2085
2400	2390



### III. Current Sensitivity

#### (1) Method

Throughout the work on the superconductivity of thin metallic films it has been noted that they were abnormally sensitive to current strength. That is, their electrical resistance, at a given temperature, was restored by currents much weaker than those called for by Silsbee's hypothesis. To determine the basis of this sensitivity, whether that of maximum current strength, maximum current density, or maximum surface density of current, the critical current was investigated for cylindrical films of the same thickness but on supports of different diameters. This is similar to the method used by Rjabinin and Schubnikow (11) for alloys; they found that the critical current was proportional to the diameter of the cylindrical sample, and consequently might be considered as a critical surface density of current.

Tin films were deposited on German silver tubes of 0.231 cm. diameter by the method described in Section II. Films of corresponding thickness were also chosen from those previously plated on German silver tubes of 0.471 cm. diameter. By selecting a third set of results taken from previous work (11) on the sensitivity to current of tin films plated on constantan wire of 0.056 cm. diameter, a good range of diameter was obtained. All the resistance measurements were made with a potentiometer, the heavy current leads being soldered to the German silver tubes and the potential leads to the tin films as before.

#### (2) Results

In tabulating the results, several facts concerning the current sensitivity of thin films should be considered. First, a suitable comparison of values for different films can be made only at a given temperature difference,  $\Delta T$ , below their respective transition points, which are different for different films. Second, the transition for higher current strengths, particularly for thin films, is much more gradual than usual for massive metal; it is therefore difficult to assign a value to the ratio  $R/R_{He}$  which will serve as a suitable criterion for the threshold current for all films. Third, the sensitivity to current is itself a property that depends upon the thickness of the film, and hence comparison should ideally be made only between films of identical thickness.

For ordinary superconducting samples the complete restoration of resistance is generally accepted as the basis for estimating the critical current. In this investigation, as soon as an appreciable portion of the resistance of the thin film has been restored, the current is divided between the film and its metal support. Hence any valid calculation of the current density in the film from the total current would be extremely difficult. In deference to the above considerations the results shown in Table IV are interpolations to constant  $\Delta T$  of the experimental results. They are tabulated for a variety of resistance ratios ( $R/R_{He}$ ) of which the smaller are probably the more reliable. For purposes of comparison the values of the critical surface density of current for "massive" tin are appended to the tables. These values are the ones which would be in agreement with Silsbee's hypothesis.

TABLE IV  
EFFECT OF ELECTRIC CURRENT ON THE SUPERCONDUCTIVITY OF TIN FILMS ON SUPPORTS OF DIFFERENT DIAMETERS AT VARIOUS TEMPERATURES BELOW THEIR TRANSITION POINTS

Thickness of film, $\mu$	Diameter of tube, cm.			Current strength (amp.) to restore $R/R_0$ to				Current density ( $10^2$ amp./cm. <sup>2</sup> ) to restore $R/R_0$ to				Surface density of current (amp./cm. <sup>2</sup> ) to restore $R/R_0$ to						
	0.47	0.23	0.056	0.01	0.05	0.10	0.50	1.00	0.01	0.05	0.10	0.50	1.00	0.01	0.05	0.10	0.50	1.00
12.2	*			10.9	12.7	13.8			6.0	7.0	7.6			7.3	8.5	9.4		
6.0		*	*	4.2	4.3	4.6	4.7	5.0	10.1	10.3	11.0	11.3	12.0	6.1	6.2	6.6	6.8	7.2
5.0		*	*			0.48					5.5				5.7			
3.7						0.53					8.2				3.0			
3.1	*			1.8	3.7	6.4			4.0	8.0	14.0			1.2	2.5	4.3		
1.7		*	*	2.7	2.9	3.0	3.2	3.5	22.5	24.6	25.0	26.8	29.7	3.8	4.2	4.3		
1.6		*	*	4.2	7.0	7.5			17.5	28.7	31.0	23.2	27.1	2.8	4.6	5.0		
1.2		*	*	1.4	1.6	1.7	1.8	2.1	17.5	19.7	21.3	23.2	27.1	2.1	2.4	2.6	2.8	3.2
1.0						0.52					29.1				2.9			
0.8		*	*	0.46	0.58	0.88	1.9	4.0	8.0	10.6	16.1	34.2	72.5	0.64	0.85	1.3	2.7	5.8
0.7			*			0.21					17.3					1.2		
0.6	*	*		0.58	1.2	1.7			6.5	13.2	19.5			0.39	0.79	1.1		
0.3 <sub>3</sub>	*	*		0.15	0.40	0.60			3.1	8.2	12.2	7.8	16.6	0.09	0.25	0.38	0.23	0.50
0.3 <sub>6</sub>		*	*	0.07	0.09	0.13	0.17	0.37	3.0	4.2	6.0			0.09	0.13	0.18		
0.3 <sub>6</sub>						0.02					5.1				0.15	0.15		

For massive tin 20.7



From these tables it is seen that a satisfactory agreement for films of the same thickness is obtained when surface density of current is taken to be their basis of current sensitivity.

#### IV. Discussion

From the results on the sensitivity of current strength it may be concluded that the restoration of resistance follows a modified Silsbee rule. That is, the return of resistance is caused by the magnetic field associated with the current, as in the case of normal superconductors, but for some reason the critical field required is very much smaller than that required when the field is applied externally.

This critical field is even smaller than that required for penetration. Fig. 5 shows the relation of the three critical fields for a typical film.  $H_1$  is the magnetic field applied externally to the superconducting film which will cause resistance to first appear in the sample.  $H_2$  is the field applied externally which will start to penetrate the still superconducting film.  $H_3$  is the field associated with the electric current which when flowing through the superconducting film will start to restore its resistance, as calculated from the data given in the "Current strength" columns of Table IV. These three apparently coincide for "massive" tin, and the critical field for tin is shown by the broken line. The relation between these three

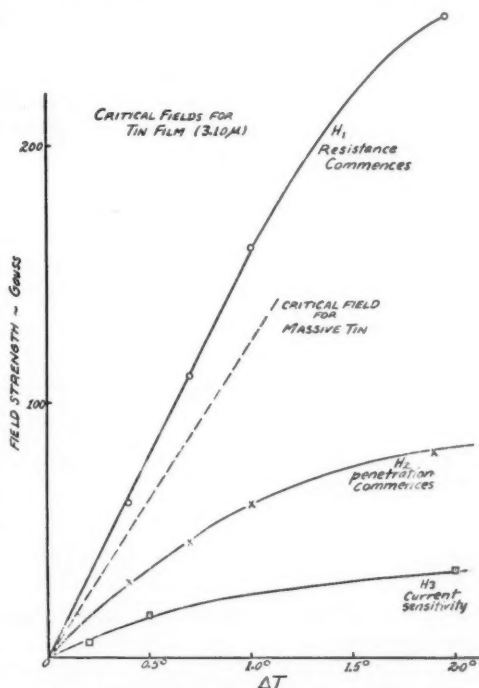


FIG. 5. Relation of the three critical magnetic fields for a superconducting tin film ( $3.10 \mu$ ).  $H_1$ —external field which will start to restore resistance.  $H_2$ —external field which will start to penetrate the film.  $H_3$ —field associated with the current which will start to restore the resistance.

critical fields is similar to that found for  $PbTi_2$  (11). The variation with temperature is not however linear. This is by no means surprising when the complex interaction of effects is considered. For example, even the very small current flowing through the samples and used to measure their resistance may profoundly affect the results. Also, as has been mentioned in previous work (9), any minute irregularities in the highly diamagnetic film will cause marked local variations in the magnetic fields.

### V. Summary

In particular the investigations here reported have shown that thin films of tin have the following anomalous behavior:

(1) Comparatively weak magnetic fields will penetrate the film before its resistance is restored by the action of the field.

(2) Their current sensitivity may be expressed in terms of a surface density of current. However, the magnetic field associated with the critical current is far less than that required for massive tin.

(3) The relative values of the three critical fields; the field required to restore resistance, the field required to penetrate the film and the field associated with the current required to restore resistance have been shown. It is seen that the films exhibit a behavior analogous to that of certain superconducting alloys. However, there is apparently no "locking in" of any of the penetrating field.

Several incidental results which are worthy of mention have emerged during the course of the investigation.

(a) The variation of transition point temperature with thickness of film was entirely in accord with previous results (2).

(b) The restoration of resistance by an external magnetic field was in agreement with previous results (9).

(c) German silver was found not to be superconducting above 2.5° K.

In their recent resume of superconductivity (13), H. Grayson Smith and J. O. Wilhelm select as a "normal" superconductor one which possesses the following properties:

(i) When in the superconducting state, it acts as a "perfect diamagnetic" towards any external magnetic field less than the threshold field as determined by experiments on the resistance.

(ii) The Meissner effect can be complete under favorable conditions of shape and purity, etc.

(iii) Silsbee's hypothesis applies to the interruption of superconductivity by heavy currents.

(iv) The specific heat anomalies are connected with the threshold magnetic fields by the thermodynamic equations of Rutgers and of Gorter and Casimir.

The above experiments have shown thin films of tin to be "anomalous" in that they fail to observe rules (i) and (iii).

### Acknowledgments

The author wishes to express his thanks to Prof. E. F. Burton, Director of the McLennan Laboratory, for making this investigation possible, and to Prof. H. Grayson Smith and Mr. J. O. Wilhelm for their continued advice and assistance.

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## A PHOTOELECTRIC PHOTOMETER<sup>1</sup>

By L. E. HOWLETT<sup>2</sup>

### Abstract

A description is given of a photoelectric photometer for measuring general light transmission through glasses, solutions, etc. It is suitable for grading where light transmission is the control. It has been successfully used to measure precisely, quickly and conveniently such quantities as the amounts of dyes removed from solutions by porous bodies, and the concentrations and purities of substances in solution.

In the course of routine work in the Optics Laboratory there has been a frequent demand for a reliable and simple method of measuring general light transmission through liquids. The name colorimeter is often improperly ascribed to an instrument measuring this property, and a problem of this nature is sometimes considered by the industrial technician to be one of colorimetry when in reality it is one of brightness rather than chromaticity. In the final analysis such problems often involve almost solely transmission or reflection. Even problems where slight changes of color are involved in industrial operations can often be reduced to simple measurements of transmission or reflection without loss of the control desired. For instance, it is desirable to sort neutral tinted wall boards. There may be some slight difference of chromaticity, but in commercial operation the main object is often merely to sort them into groups of a small range of difference, whether it be in chromaticity or in brightness. The treatment thus becomes easier and simpler.

Many of these problems of transmission of light are not directly linked with the visibility curve of the eye. By this is meant that it is desired to observe relative differences between samples of the same color and not to measure those relative differences which the eye sees. In fact, given a pair of samples which differ little to the eye, it may be possible to increase the apparent difference between them according to the readings of an instrument of which the response curve occupies a part of the spectrum different from that occupied by the visibility curve of the eye. Often the absorption bands of dye solutions are very sharp. If the combined response of the cell and filter is made to cover approximately this region, the readings of the instrument will give differences between different samples which are greater than would be observed by the eye alone. This has already been found extremely useful in certain work involving the removal of dyes from solutions by various absorbing materials. The instrument described here makes such tests easier, quicker, and relatively more reliable than visual observations. This makes the employment of a photocell a very satisfactory arrangement from a practical point of view. In cases where measurements must definitely be in terms of the visibility

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curve of the eye, it is not too difficult a task to compensate the response of the cell to that of the eye, by means of a suitable filter, to a degree that will meet the requirements of most commercial and large-scale operations.

The continual necessity of making transmission measurements of this type in a convenient and accurate manner has led to the development of this instrument for the purpose in the Optics Laboratory. The requirements of such an apparatus have been formulated from the various tasks which it has been called upon to perform. These may be briefly stated as follows:—

(1) That it shall be simple and easy to operate, so that it is safe in the hands of comparatively unskilled workers.

(2) That it be reliable to as high a degree as possible in its readings, and that it maintain its precision over long periods of time.

(3) That it be immune to temperature effects caused by the lighting system, location, etc.

(4) That the effect of fatigue be limited to the minimum so that accurate measurements may be taken on highly transparent and very dense solutions without delay.

(5) That it should be as rugged as possible compatible with the previous requirements.

First efforts were directed towards utilization of commercial barrier plane cells because of the simplicity of operation which is inherent in their use, owing to the absence of batteries, but it was found that these cells were too susceptible to fatigue and temperature changes for the reliability which was sought for the type of work under consideration. Accordingly, after preliminary experimentation it was decided that a vacuum photoelectric cell best fulfilled the requirements set forth. Since it was required that the instrument be fairly rugged and that readings should be made on a not too sensitive instrument, a stage of amplification was necessary. This amplifier, as can be seen from Fig. 1, has been kept as simple as possible. That it is not too complicated for commercial operation has been demonstrated by the fact that it has been used successfully by untrained operators after a few minutes' instruction. The present model employs batteries but a new design is planned to avoid these.

Since it was desired to prevent any variations of the amplifier over a period of time from affecting the measurements, the manner of taking them was to compensate the photoelectric current by appropriately changing the potential across the grid-coupling resistance by means of a potentiometer set on the panel of the instrument. This change of voltage is taken as a measure of the photo current. The reliability of the whole arrangement then depends only upon the linearity of the vacuum photocell and the permanence of its properties. This seems to be the limit of accuracy to which one can conveniently work without calibrating the photocell. The batteries do not in any way affect results as the potential drops, until they are so poor that rapid fluctuations of voltage take place. The diagram of the circuit is shown in Fig. 1.

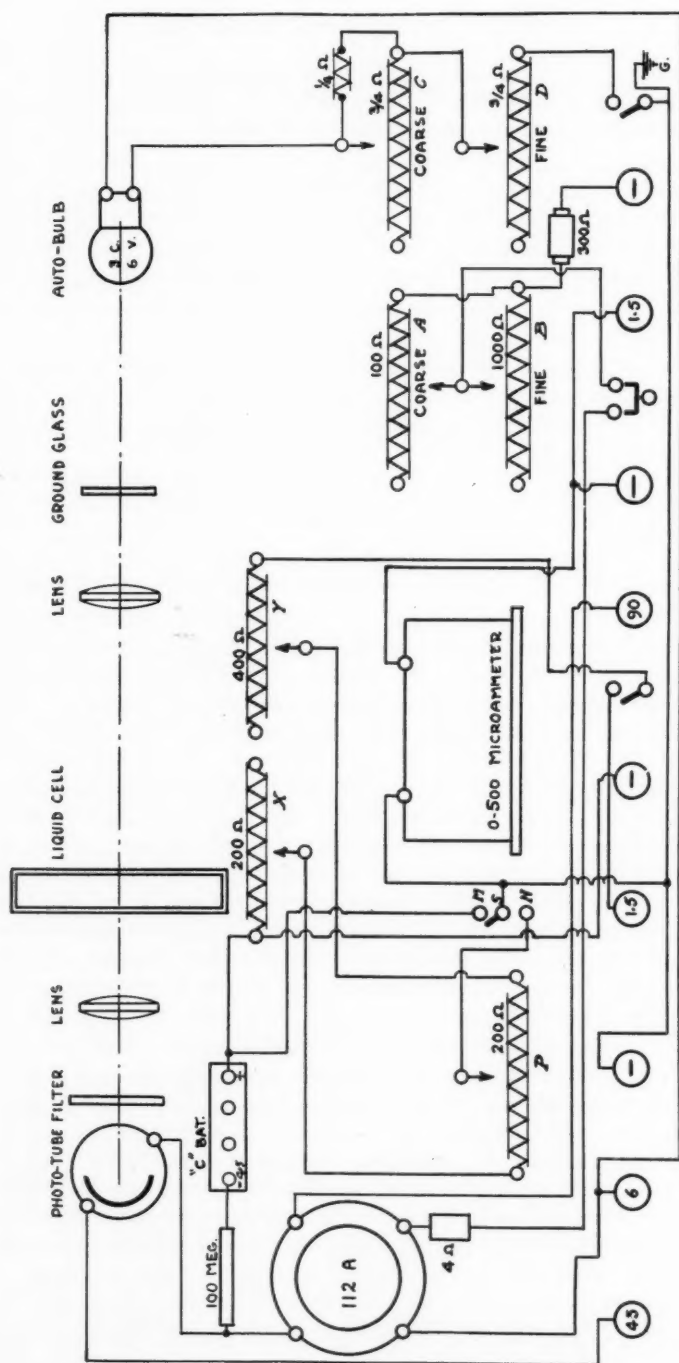


FIG. 1. Photodetector cell.

The effective response curve of the photocell is so adjusted by the use of filters that it is the most suitable for the particular work for which the instrument is required, and may be fairly readily changed if the requirements are different for different types of work. The aim in this matter may be either: (i) to make the difference between the readings for two samples as great as possible by choosing the appropriate part of the spectrum after considering the sensitivity curve of the cell, the absorption band of the liquid and emission curve of the source; or (ii) to reproduce the visibility curve of the eye so that percentage transmissions as read by the instrument are on this basis.

Fig. 1 is practically self-explanatory. The mode of operation is simple. The front panel contains resistance *A*, *B*, *C* and *D*, the microammeter, the grid potentiometer, *P*, and the various switches. The two calibration resistances, *X* and *Y*, are within the shielded box and are operated by means of a screw driver inserted through a hole. For ordinary use, calibration resistance *X* is set at zero resistance and the calibration resistance *Y* at a value such that approximately sufficient voltage is available on the grid potentiometer to compensate the photocell when light falls on it directly from the lamp. The instrument is first balanced so that the microammeter in the plate circuit reads zero with a shutter between the light source and the photoelectric cell. This is done by the adjustment of resistances *A* and *B*, with switch *S* in position *M*. The shutter is then removed, the switch *S* placed in position *N* and the grid potentiometer set at its maximum potential to represent 100% transmission. A blank cell containing distilled water is placed between the photocell and the light source, and the last-named is adjusted by rheostats *C* and *D* so that the microammeter in the plate circuit again reads zero. Intermediate points can then be calibrated on the grid potentiometer, assuming only the linearity of the response of the photoelectric cell and the uniformity of the resistance of the potentiometer, both of which can be readily checked. Percentage transmissions may then be read directly from the grid potentiometer by inserting the cell of liquid to be tested, instead of the cell of distilled water, and restoring the photoelectric current to zero by means of the potentiometer *P*. These percentages of general transmission will of course be in terms of the response curve of the photocell and filter combination. This response curve, as indicated previously, may be adjusted to whatever is desired within wide limits. Under some circumstances it is desirable to calibrate the potentiometer not in terms of transmission but in quantity of solute. Often when a transmission test is to be used as a control, it is necessary to study only a portion of the percentage transmission range. The two calibration resistances, *X* and *Y*, can be set so as to bring only a given portion of the transmission range on to the scale of the grid potentiometer on the front panel. When this range does not include 100% transmission and when once the grid potentiometer has been calibrated, future checks on the light source can be made with a standard solution or with a standard aperture instead of the cell of distilled water. Several improvements have been recently made on the present model; the most important of these is to have a

rotating cylinder as the liquid cell carrier such that it automatically controls the switch *S*. There are three positions to which the carrier can be rotated. The axis of the light beam intersects the axis of the cylinder at right-angles, and about the circumference of the cylinder are holders for (a) a shutter, (b) the cell containing the standard liquid or an aperture and (c) the cell containing the liquid of unknown transmitting power.

The three positions of this cylindrical carrier result in the following conditions at the three settings:—

- (a) A shutter intercepts the beam of light.
- (b) A cell of distilled water (or a standard solution or aperture, if a limited range of middle transmissions is required) obstructs the beam of light.
- (c) The cell containing the liquid to be measured is in the beam of light.

For position (a) the switch will be in position *M*, and for positions (b) and (c) of the liquid cell carrier the switch *S* will be in the position *N*.

It might be emphasized that the switch *S* should be of very reliable construction and very positive in its action. Some trouble was encountered in early design by using a double throw radio toggle switch. This was discarded for one constructed for the purpose, of simpler form and very positive in its action. The potentiometers and rheostats should also be of a very dependable type in order to ensure stability of operation.

In concluding it might be said that the completed instrument fulfils very well the conditions laid down for it and has proved extremely reliable in practical operation. The current amplification of the circuit as it stands is about  $10^6$ . This can be increased if the occasion requires by increasing the value of the grid coupling resistance. A current amplification of close to  $10^7$  can be obtained by careful adjustment. The sensitivity of the vacuum photocell is rated at four microamperes per lumen.

## THE SPECTRUM OF TREBLY IONIZED THORIUM<sup>1</sup>

BY R. J. LANG<sup>2</sup>

### Abstract

An analysis of the spectrum of Th IV is given which includes practically all the stronger known lines of thorium which can be attributed to the trebly ionized atom. This spectrum all lies on the short wave-length side of 2350Å, with the exception of one line, 7S—7P, which falls at  $\lambda 2694.00\text{\AA}$ . Most of the lines of the spectrum above 2000Å are quite intense in the spark in air, but do not appear at all in the arc and are definitely enhanced in the vacuum spark. The separation of the deepest 7P terms has the relatively enormous value of  $12818\text{ cm}^{-1}$ . The terms 7P, 6D, 7D, 8D, 7S, 8S, 9S, 5F and 5G have been found. The ionization potential of Th<sup>+++</sup> is approximately 29.4 volts.

### Experimental Procedure

Several years ago the writer became interested in the spectrum of Th IV and photographed the vacuum spark from about 3000Å down to 1000Å, and discovered a small number of outstanding lines lying in the region between 2200 and 1500Å which were thought to belong to the one-electron spectrum. Not much progress could be made at that time on account of the lack of accurate standards of wave-lengths in the 2000Å region. From time to time, following this preliminary survey, the measurements were extended into the far ultra-violet to 350Å and up to 4000Å and the accuracy improved, especially when it became possible to use the excellent wave-lengths of carbon, oxygen and nitrogen made by Edlen (1) not only for the extreme ultra-violet region, but, by means of their higher orders, for the 2000Å region as well. The spectrum was finally photographed in the arc and spark in air or nitrogen, as well as the vacuum spark between 4000Å and 1500Å and the vacuum spark alone from 1500Å down to 350Å. The pole effect was tried on the group of outstanding lines mentioned above and the results of this, combined with the fact that all these lines are absent from the arc spectrum, confirmed the earlier conclusion that these were the lines of the Th IV spectrum. The analysis still would have been very difficult if not impossible without the knowledge which was obtained meanwhile concerning the spectrum of Ra II (4) and Ce IV (3).

### Theoretical Considerations

The steady trend of the principal doublet S - P toward the red with increasing atomic number in the spectra of the homologous ions, Ti IV (5) Zr IV (2) and Ce IV, suggested that in Th IV the longer line of the pair would lie well on the red side of 3000Å. The failure to find any such line which could be attributed to this ion was at first very puzzling, but the information concerning the spectrum of Ra II cleared up this difficulty by showing that the introduction of the completed shell of fourteen *f* electrons, as the rare earth

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group develops, results in a reversal of this red-ward trend so that in Ra II, allowing for a greatly increased interval between the two lines, this doublet falls in about the same place as in Ca II. There is but one line of any marked intensity longer than 2350Å which can be attributed to Th IV. It lies at 2694.00Å. It shows all the characteristics of the other strong lines lying between 2350 and 1500Å which were considered by the writer to constitute the spectrum in question.

Various early estimates of the interval of the 7P terms had led the writer to expect a very large value in the neighborhood of 10,000 cm.<sup>-1</sup>, but the only reasonable value which could be obtained from the spectrum involving the line at 2694.00 was 12816 cm.<sup>-1</sup>. In private discussion last summer

TABLE I  
PRINCIPAL DOUBLET SEPARATIONS

Ion		Interval	Z	Z <sup>2</sup>	$\frac{\Delta\nu}{Z^2}$
Ca	II	223	20	400	0.558
Sr	II	801	38	1444	0.555
Ba	II	1691	56	3136	0.539
Ra	II	4857	88	7744	0.627
Sc	III	474	21	441	1.075
Yt	III	1553	39	1521	1.021
La	III	3095	57	3249	0.953
Ac	III	(8317)	89	7921	(1.05)
Ti	IV	818	22	484	1.688
Zr	IV	2483	40	1600	1.555
Ce	IV	4707	58	3364	1.399
Th	IV	12818	90	8100	1.582

with Dr. Whitford at the California Institute of Technology, the writer learned that he also had arrived at the same two lines as representing the 7S - 7P doublet. Here again confirmation was obtained from the Ra II spectrum as shown in Table I. In the last column it will be observed that while the doublet interval, divided by the square of the atomic number Z, steadily decreases in the usual manner as far as Ba II, there is a sharp rise at Ra II. A similar but not quite so marked rise occurs at Th IV.

If one applies the regular doublet formula

$$\Delta\nu = \frac{R\alpha^2(Z-S)^4}{n^2l(l+1)}$$

to Ra II and Th IV, the entirely reasonable values of 63.5 and 58.8 are obtained for the screening constant.

The interval 12818 cm.<sup>-1</sup> occurs several times between pairs of Th IV lines, thus making it possible to locate tentatively some of the important multiplets. Table II shows the analysis of the spectrum and the terms based upon zero value for the deepest term 6s<sup>2</sup>6p<sup>6</sup>6d<sup>2</sup>D<sub>2</sub>. Where the lines of a given multiplet are so widely separated it is quite difficult to make any accurate judgment of relative intensity, and in this case the difficulty is further increased by the fact that in such a multiplet as 7P - 7D, one line lies in the vacuum region while the other two lie at about 2000Å. The intensities given are visual estimates from vacuum spark plates in all cases except 5F - 5G and 5F - 8D. Even then, since the vacuum spectrograph covers only about



600Å at one exposure, the lines usually lie on separate plates which were taken at different times and with unavoidable differences of exposure and development.

TABLE II  
CLASSIFIED LINES IN Th IV

Combination	$\lambda$ I.A. Int.	Wave number and interval	Term values
7S <sub>1</sub> - 7P <sub>2</sub>	2002.38(10)	49924.5	
7S <sub>1</sub> - 7P <sub>1</sub>	2694.00(30)	37108.5	6D <sub>2</sub> 0
			6D <sub>3</sub> 5292 5292
6D <sub>2</sub> - 7P <sub>1</sub>	1959.05(40)	51045.1	
6D <sub>3</sub> - 7P <sub>2</sub>	1707.33(30)	58571.0	7S <sub>1</sub> 13938
6D <sub>2</sub> - 7P <sub>2</sub>	1565.85(15)	63863.1	
			7P <sub>1</sub> 51045
5F <sub>3</sub> - 5G <sub>4</sub>	2308.43 (5)	43306	7P <sub>2</sub> 63863 12818
5F <sub>4</sub> - 5G <sub>3</sub>	2337.33(10)	42771	
5F <sub>4</sub> - 5G <sub>4</sub>	2337.92 (2)	42760	
			7D <sub>2</sub> 110491
			7D <sub>3</sub> 112233 1742
5F <sub>3</sub> - 8D <sub>2</sub>	2317.11 (5)	43144.0	
5F <sub>4</sub> - 8D <sub>3</sub>	2296.80 (6)	43525.4	8S <sub>1</sub> 116903
5F <sub>3</sub> - 8D <sub>3</sub>	—	(44068)	
			5F <sub>3</sub> 118076
7P <sub>2</sub> - 7D <sub>2</sub>	2144.00 (8)	46627.0	5F <sub>4</sub> 118620 544
7P <sub>2</sub> - 7D <sub>3</sub>	2066.75(20)	48369.7	
7P <sub>1</sub> - 7D <sub>2</sub>	1682.17(15)	59447.0	8D <sub>2</sub> 161221
			8D <sub>3</sub> 162144 923
7P <sub>2</sub> - X	2146.79(12)	46566	
7P <sub>1</sub> - X	1683.96(12)	59384	9S <sub>1</sub> 162172
7P <sub>2</sub> - 8S <sub>1</sub>	1885.40 (5)	53039	5G <sub>4</sub> 161381
7P <sub>1</sub> - 8S <sub>1</sub>	1518.38 (9)	65859	5G <sub>3</sub> 161391 10
7P <sub>2</sub> - 8D <sub>2</sub>	1027.15 (2)	97357	X 110429
7P <sub>2</sub> - 8D <sub>3</sub>	1017.50 (8)	98280	
7P <sub>1</sub> - 8D <sub>2</sub>	907.63 (7)	110177	
7P <sub>2</sub> - 9S	1017.19 (8)	98310	
7P <sub>1</sub> - 9S	899.88 (5)	111126	
6D <sub>2</sub> - 5F <sub>3</sub>	846.91(30)	118076	
6D <sub>3</sub> - 5F <sub>4</sub>	882.39(30)	113328	
6D <sub>2</sub> - 5F <sub>3</sub>	886.66(12)	112783	



The 6D - 5F multiplet is outstanding on the plates and its discovery just in the expected position confirmed the correctness of the general scheme. There is no way at present of confirming the interval of the 7D terms, as its combination with 5F is beyond the range of the author's apparatus and 6F has not yet been found. There is one pair of lines with the 7P interval exactly, which give a term value denoted by X close to the value of 7D. It was thought at first that this term was 8S, but if that is true, the 8D and 9S terms can hardly be correct and 8D seems well established. It seems impossible to find the 8P terms, nor have they been found in Zr IV or Ce IV.

The G terms may not be quite certain. They are not quite so hydrogenic as might be expected. So many strong lines occur in the region where the G-H lines should fall that it will be difficult to find them if they are as weak as they are in Ti IV.

### Series Limits and Ionization Potential

The three S terms are closely represented by the Ritz formula

$$mS = \frac{16R}{[m - 4.1829 - 8.12 \times 10^{-8}(mS)]^2}$$

where  $m$  takes the values 7, 8 and 9. The term values referred to the limit of this series with the Rydberg denominators  $n^*$  are given in Table III. The value of the deepest term leads to an ionization potential of 29.38 volts. This may be compared with 33.83 for Zr IV (2) and 30.42 for Ce IV (3).

TABLE III  
TERM VALUES AND RYDBERG DENOMINATORS

Term value		$n^*$	Term value		$n^*$
7S <sub>1</sub>	224097	2.7991	6D <sub>2</sub>	238035	2.7159
8S <sub>1</sub>	121132	3.8073	6D <sub>3</sub>	232743	2.7466
9S <sub>1</sub>	75863	4.8109			
			7D <sub>2</sub>	127544	3.7072
7P <sub>1</sub>	186990	3.0643	7D <sub>3</sub>	125802	3.7360
7P <sub>2</sub>	174172	3.1751			
			8D <sub>2</sub>	76814	4.7809
5F <sub>3</sub>	119959	3.8258	8D <sub>3</sub>	75891	4.8100
5F <sub>4</sub>	119415	3.8345			
			5G <sub>4</sub>	76654	4.7859
			5G <sub>5</sub>	76644	4.7862

### Note on the Spectrum of Ac III

It seems possible with the information available for the spectra of Ra II and Th IV to make an approximate estimate of one or two things connected with the spectrum of Ac III. For example, the regular doublet formula used above will give a rough estimate of the separation of the 7 P terms. If  $S$  is given the value 61.0, an interval of 8290 cm.<sup>-1</sup> is obtained. If, on the other

hand, we refer to Table I it is shown that when we allow a rise in the value of  $\frac{\Delta\nu}{Z^2}$  similar to that in Ra II or Th IV, we get a value of 8317 cm.<sup>-1</sup>. It seems clear from these two results that this interval cannot be very different from 8300 cm.<sup>-1</sup>. The positions of these two strong lines 7S - 7P can also be roughly predicted by the use of  $\sqrt{\frac{\nu}{R}}$  for Ra II and Th IV, for the three term values involved. This suggests that these lines will occur in the neighborhood of 2650 and 3450Å. The ionization potential will be close to 20 volts and the deepest term 6D<sub>2</sub> will have a value, therefore, in the neighborhood of 165,000 cm.<sup>-1</sup>.

#### Note on the Spectra of La III and Ce IV

Owing to the general interest which attaches to the F terms of La III and Ce IV, the author takes this opportunity to state that it seems very probable that the D - F multiplet given for La III (3) should have been assigned to the 5F terms instead of 4F as follows:

5D <sub>2</sub> - 5F <sub>3</sub>	1081.61(15)	92454.7	1603.4 80.1
5D <sub>3</sub> - 5F <sub>4</sub>	1099.73(15)	90931.4	
5D <sub>3</sub> - 5F <sub>3</sub>	1100.70 (7)	90851.3	

The corresponding multiplet in Ce IV is given by the following lines:

5D <sub>2</sub> - 5F <sub>3</sub>	741.79(40)	134809	2490 201
5D <sub>3</sub> - 5F <sub>4</sub>	754.60(30)	132520	
5D <sub>3</sub> - 5F <sub>3</sub>	755.75(12)	(132319)	

The F terms from this assignment correspond well with those in the other homologous spectra, Ti IV, Zr IV and Th IV.

#### Acknowledgment

The writer takes pleasure in thanking Dr. H. N. Russell for his instructive and kindly criticism of the results of the analysis of the Th IV spectrum; and Dr. R. E. Meyers of the Westinghouse Lamp Co., for supplying him with the thorium metal. He also wishes to acknowledge the assistance of Mr. J. S. Beggs in taking some of the photographs.

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## PROPAGATION AND RESONANCE OF LONGITUDINAL WAVES IN PRISMATIC RODS<sup>1</sup>

By R. RUEDY<sup>2</sup>

### Abstract

For vibrations involving shearing and rotation, and for those involving both distortion and dilatation, the equations of motion combined with the boundary conditions yield in the simplest case a cubic equation for the resonance frequencies; its solution depends on Poisson's ratio and on the resonance frequencies  $f_x$ ,  $f_y$ ,  $f_z$ , which the rod possesses when in pure shearing motion in the direction of its three axes. Three series of resonance frequencies are obtained when  $f_y$  and  $f_z$  are constant and the frequencies of the overtones are inserted for  $f_x$ . A fourth series of resonance frequencies begins above the highest of the fundamental frequencies  $f_x$ ,  $f_y$ ,  $f_z$ .

### Introduction

When waves of very high frequency are set up in prismatic bars, the resulting motions present an almost endless variety of combinations (3, 5). The manifold resonances revealed by experiment have until now rendered unsuccessful the attempts to ascertain the laws governing the possible resonance frequencies. These vibrations, on the other hand, have proved to be one of the most regular mechanical motions that it is possible to produce and maintain by artificial means. The precision of quartz rod clocks rivals, if it does not actually surpass, the greatest precision of astronomical determinations. One of the first clocks of this kind, already in use for giving scientific and industrial laboratories accurate time signals, has been in continuous operation for nearly two years, keeping time to within about 0.002 sec. and making possible an accuracy in signals transmitted by radio of  $\pm 0.02$  sec. during several months. The controlling element in this particular clock is a quartz rod (Fig. 1), so placed that its greatest dimension, 91 mm., is in the direction of the electrical axis, in order to reduce the influence of changing temperature and of overtones; it is caused to vibrate at 60,000 cycles per sec., the frequency of its fourth harmonic, and is firmly held in place at the nodes (1). The comparison of a few quartz clocks has revealed changes in the speed of rotation of the earth (6).

More recently, transparent vibrating prismatic rods have been used for the determination of elastic constants, and for studying the propagation of ultrasonic waves in liquids (3). In order to use the rods to best advantage, a detailed knowledge of the vibrating motion and of the resonance frequencies is required.

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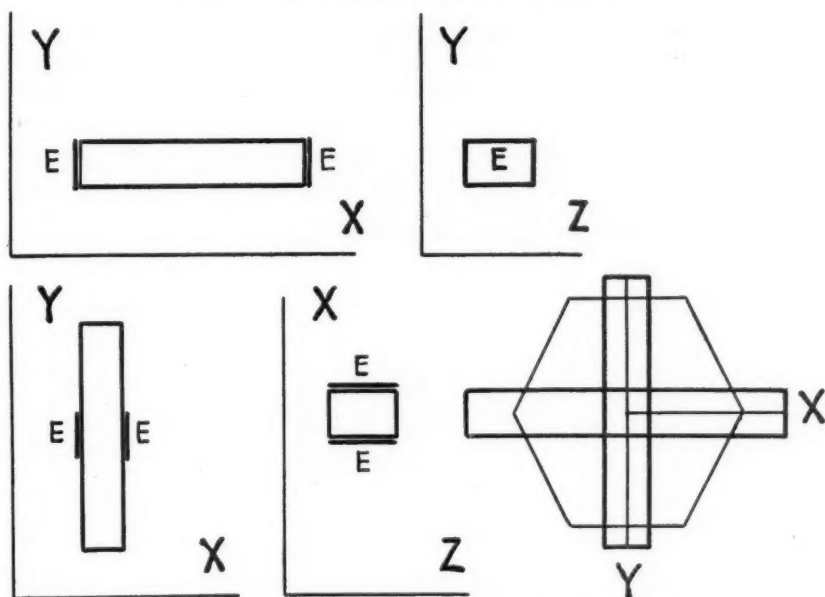


FIG. 1. Orientation of quartz rods set into vibration by the electric field ( $X$ , electrical axis;  $Z$ , optical axis;  $Y$ , neutral axis;  $E$ , electrodes). The orientation shown in the upper half of the figure is less liable to be affected by overtones.

### Wave Equations for the Elastic Solid Body

When the velocity of longitudinal waves in a bar is deduced, it is usual to consider merely the difference in the forces of compression at two neighboring cross sections. Let  $u$  be the longitudinal displacement in the direction of the longest dimension,  $x$ , at the first cross section; the unit elongation is  $\partial u / \partial x$ , and the tensile stress per unit area is  $E \partial u / \partial x$ , where  $E$  is Young's modulus of elasticity. Since  $E$ , as ordinarily measured and defined, includes the force for producing lateral contraction,  $C = (E / \rho)^{1/2}$ , the velocity of propagation of longitudinal waves in a rod made of a material of density  $\rho$ , is smaller than the velocity  $c_1 = (E(1 - \sigma) / \rho(1 + \sigma)(1 - 2\sigma))^{1/2}$ , of a narrow beam of waves in an infinite medium, where the unavoidable lateral motion is prevented or greatly reduced by the masses surrounding the track of the waves. The forces arising from the motion of particles in a lateral direction, the displacements being determined by Poisson's ratio of the material, are however neglected in the case of bars, a justifiable procedure so long as waves of low frequency are considered. But for sound of very short wavelength, the cycles of lateral expansion and contraction may be expected to create new conditions of resonance, and to decrease still further the velocity of propagation of longitudinal waves. The effect produced may be ascertained by examining the complete equations of motion.

Let the components of the small displacement along the three axes at any point  $x, y, z$ , in a solid be designated by  $u, v, w$ , respectively. When internal stresses exist, or are momentarily created in the bar, the motions produced obey the equations (4):

$$\begin{aligned}\rho \frac{\partial^2 u}{\partial x^2} &= \left(k + \frac{G}{3}\right) \frac{\partial e}{\partial x} + G \nabla^2 u = (\lambda + G) \frac{\partial e}{\partial x} + G \nabla^2 u \\ \rho \frac{\partial^2 v}{\partial y^2} &= \left(k + \frac{G}{3}\right) \frac{\partial e}{\partial y} + G \nabla^2 v = (\lambda + G) \frac{\partial e}{\partial y} + G \nabla^2 v \\ \rho \frac{\partial^2 w}{\partial z^2} &= \left(k + \frac{G}{3}\right) \frac{\partial e}{\partial z} + G \nabla^2 w = (\lambda + G) \frac{\partial e}{\partial z} + G \nabla^2 w,\end{aligned}$$

where

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

$$k = \frac{E}{3(1-2\sigma)}, \text{ is the modulus of volume elasticity,}$$

$$G = \frac{E}{2(1+\sigma)}, \text{ is the modulus of rigidity or shearing elasticity,}$$

$$\lambda = \frac{E\sigma}{(1+\sigma)(1-2\sigma)}, \text{ is an elastic constant,}$$

$$e = \frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z}, \text{ is the volume expansion.}$$

If the vibrations produced in the rod are such that the volume expansion,  $e$ , is zero,

$$\nabla^2 u = \frac{\rho}{G} \frac{\partial^2 u}{\partial t^2}$$

$$\nabla^2 v = \frac{\rho}{G} \frac{\partial^2 v}{\partial t^2}$$

$$\nabla^2 w = \frac{\rho}{G} \frac{\partial^2 w}{\partial t^2};$$

the corresponding waves are called waves of distortion, and involve shearing distortion and rotation only.

On the other hand, when the deformation produced by the waves is free from rotation, the following expressions must vanish:

$$\omega_x = \frac{1}{2} \left( \frac{\partial w}{\partial y} - \frac{\partial v}{\partial z} \right) \quad \omega_y = \frac{1}{2} \left( \frac{\partial u}{\partial z} - \frac{\partial w}{\partial x} \right) \quad \omega_z = \frac{1}{2} \left( \frac{\partial v}{\partial x} - \frac{\partial u}{\partial y} \right).$$

The equations are always satisfied if a function,  $\Psi$ , exists from which  $u$  is found by differentiation with respect to  $x$ ,  $v$  by differentiation with respect to  $y$ , and  $w = \partial \Psi / \partial z$ . Then the general equations become

$$\nabla^2 u = \frac{\rho}{\lambda + 2G} \frac{\partial^2 u}{\partial t^2}$$

$$\nabla^2 v = \frac{\rho}{\lambda + 2G} \frac{\partial^2 v}{\partial t^2}$$

$$\nabla^2 w = \frac{\rho}{\lambda + 2G} \frac{\partial^2 w}{\partial t^2}.$$

These equations represent waves of dilatation.

# Frequency Equations

## a. Waves of Dilatation

A simple function which represents a harmonic motion and satisfies the conditions for absence of rotation is

$$\Psi = -i(Ae^{i\alpha x} + Be^{i\beta y} + Ce^{i\gamma z})e^{ipt}$$

The equation of motion leads to the relation

$$\frac{\lambda+2G}{\rho}\alpha^2 = c_1^2\alpha^2 = c_1^2\beta^2 = c_1^2\gamma^2 = p^2.$$

When the displacements  $u, v, w$  are each functions of  $x, y, z$ , an appropriate expression is furnished by

$$\Psi = -iAe^{i(\alpha x + \beta y + \gamma z)}e^{ipt},$$

so that

$$u = \alpha A e^{i(\alpha x + \beta y + \gamma z)}e^{ipt}$$

$$v = \beta A e^{i(\alpha x + \beta y + \gamma z)}e^{ipt}$$

$$w = \gamma A e^{i(\alpha x + \beta y + \gamma z)}e^{ipt}.$$

The equations of motion lead to the equation for the frequency, i.e.,

$$p^2 = \frac{\lambda+2G}{\rho}(\alpha^2 + \beta^2 + \gamma^2),$$

in which  $\alpha, \beta$  and  $\gamma$  are arbitrary constants.

## b. Waves of Distortion

The equations of motion are satisfied by the slightly more general expressions

$$u = A_1 e^{i(\alpha x + \beta y + \gamma z)}e^{ipt}$$

$$v = A_2 e^{i(\alpha x + \beta y + \gamma z)}e^{ipt}$$

$$w = A_3 e^{i(\alpha x + \beta y + \gamma z)}e^{ipt}$$

on condition that, with  $\rho c_2^2 = H$ , where  $H$  depends on the frequency, and must be determined from the general equations of motion,

$$\left(\alpha^2 - \frac{p^2}{c_2^2}\right) + b^2 + c^2 = 0 \quad \text{for } u$$

$$a^2 + \left(\beta^2 - \frac{p^2}{c_2^2}\right) + c^2 = 0 \quad \text{for } v$$

$$a^2 + b^2 + \left(\gamma^2 - \frac{p^2}{c_2^2}\right) = 0 \quad \text{for } w.$$

Treating these relations as if they were three homogeneous equations, it follows that

$$\begin{vmatrix} \alpha^2 - \frac{p^2}{c_2^2} & b^2 & c^2 \\ a^2 & \beta^2 - \frac{p^2}{c_2^2} & c^2 \\ a^2 & b^2 & \gamma^2 - \frac{p^2}{c_2^2} \end{vmatrix} = 0$$

or

$$\frac{p^4}{c_2^4} - \frac{p^4}{c_2^4}(\alpha^2 + \beta^2 + \gamma^2) + \frac{p^2}{c_2^2}(\alpha^2\beta^2 + \beta^2\gamma^2 + \alpha^2\gamma^2 - a^2b^2 - b^2c^2 - a^2c^2) - 2a^2b^2c^2 - \alpha^2\beta^2\gamma^2 + \alpha^2b^2c^2 + \beta^2a^2c^2 + \gamma^2a^2b^2 = 0.$$

When  $a$  is chosen equal to  $\alpha$ ,  $b = \beta$ , and  $c = \gamma$ , the expression reduces to

$$\frac{p^2}{c_s^2} = \alpha^2 + \beta^2 + \gamma^2,$$

as in the case of the waves of dilatation. In this case  $c_s^2 = G/\rho$  and  $e = 0$ .

### c. Complete Waves

When the waves produce both dilatation and shearing distortion, the following solutions are suitable:

$$\begin{aligned} u &= A_1 e^{i(\alpha x + \beta y + \gamma z)} e^{i p t} \\ v &= A_2 e^{i(\alpha x + \beta y + \gamma z)} e^{i p t} \\ w &= A_3 e^{i(\alpha x + \beta y + \gamma z)} e^{i p t} \end{aligned}$$

On introducing them into the three general equations of motion, three relations are obtained which are valid concurrently only when the determinant vanishes, or when, with

$$\begin{aligned} (\alpha^2 + \beta^2 + \gamma^2) \frac{G}{\rho} &= (\alpha^2 + \beta^2 + \gamma^2) c_s^2 = p_s^2 + p_y^2 + p_z^2 = S^2, \\ \left(\frac{p}{S}\right)^6 - \left(\frac{p}{S}\right)^4 \left(3 + \frac{\lambda + G}{G}\right) + \left(\frac{p}{S}\right)^2 \left(3 + 2 \frac{\lambda + G}{G}\right) - \frac{\lambda + 2G}{G} &= 0 \end{aligned}$$

or

$$\left(\frac{p}{S}\right)^6 - 2 \left(\frac{p}{S}\right)^4 \frac{2-3\sigma}{1-2\sigma} + \left(\frac{p}{S}\right)^2 \frac{5-6\sigma}{1-2\sigma} - \frac{2(1-\sigma)}{1-2\sigma} = 0.$$

This equation always gives at least one real solution for the ratio  $p^2/S^2$

A more general solution is obtained by again making use of the parameters  $a$ ,  $b$ ,  $c$ , in addition to  $\alpha$ ,  $\beta$ ,  $\gamma$ .

### Influence of Boundary Conditions

The frequencies found to be compatible with the general equations of motion of the elastic solid body have furthermore to satisfy the boundary conditions; that is, in the absence of external forces, all the stresses over the surfaces of the prism vanish.

The normal stress or pressure per unit area on any plane perpendicular to the  $x$ -axis is denoted by  $X_x$ ; it acts in the direction of  $x$ ; the tangential stresses in the same plane are designated  $Y_x$  and  $Z_x$ , depending upon the direction. The corresponding quantities for planes parallel to  $x$ ,  $z$  are  $Y_y$ ,  $X_y$  and  $Z_y$ . By considering the stresses acting upon the faces of an element of volume, and by applying Hooke's law for the elastic deformation produced, the following equations are obtained (4):

$$\begin{aligned} X_x &= (k - \frac{2}{3}G)e + 2G \frac{\partial u}{\partial x} = \lambda e + 2G \frac{\partial u}{\partial x} \\ Y_y &= (k - \frac{2}{3}G)e + 2G \frac{\partial v}{\partial y} = \lambda e + 2G \frac{\partial v}{\partial y} \\ Z_z &= (k - \frac{2}{3}G)e + 2G \frac{\partial w}{\partial z} = \lambda e + 2G \frac{\partial w}{\partial z} \end{aligned} \quad e = \frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z}$$



The shearing strains  $\partial v/\partial x + \partial u/\partial y$ ,  $\partial w/\partial x + \partial x/\partial z$ , and  $\partial w/\partial y + \partial v/\partial z$  are given by the equations:

$$Y_x = X_y = G\left(\frac{\partial v}{\partial x} + \frac{\partial u}{\partial y}\right) \quad X_z = Z_x = G\left(\frac{\partial w}{\partial x} + \frac{\partial u}{\partial z}\right) \quad Y_z = Z_y = G\left(\frac{\partial w}{\partial y} + \frac{\partial v}{\partial z}\right).$$

When the prism is bounded by the planes  $x=0$  and  $x=l$ ,  $y=0$  and  $y=m$ ,  $z=0$  and  $z=n$ , the following relations must hold:

$$\begin{aligned} X_x &= Y_x = Z_x = 0 \quad \text{at } x = 0 \quad \text{and } x = l \\ Y_y &= X_y = Z_y = 0 \quad \text{at } y = 0 \quad \text{and } y = m \\ Z_z &= X_z = Y_z = 0 \quad \text{at } z = 0 \quad \text{and } z = n. \end{aligned}$$

Since all the variable terms entering into the expressions for the normal and tangential forces consist of first derivatives, all the boundary conditions are directly satisfied if in the equations for  $u$ ,  $v$ ,  $w$  the exponential functions are replaced by  $\cos \alpha x \cos \beta y \cos \gamma z$  or  $\sin \alpha x \cos \beta y \cos \gamma z$  or by similar expressions, provided that

$$\alpha = 2\kappa_1 \frac{\pi}{2l}, \quad \beta = 2\kappa_2 \frac{\pi}{2m}, \quad \gamma = 2\kappa_3 \frac{\pi}{2n} \quad \text{for cosine terms}$$

or

$$\alpha = (2\kappa_1 + 1) \frac{\pi}{2l}, \quad \beta = (2\kappa_2 + 1) \frac{\pi}{2m}, \quad \gamma = (2\kappa_3 + 1) \frac{\pi}{2n} \quad \text{for sine terms,}$$

where  $\kappa_1$ ,  $\kappa_2$  and  $\kappa_3$  may be any whole number. The letters  $\alpha$ ,  $\beta$ , and  $\gamma$ , and similarly  $a$ ,  $b$  and  $c$ , are thus seen to represent the length of the standing waves, while the equations of motion determine the frequencies. The wave motion is therefore completely fixed.

For pure dilatational waves, the resonance frequency becomes equal to the square root of the three frequencies the rod would have when vibrating in the direction of its length, width or height. Since width and height are small compared with the length, and the frequencies corresponding to the vibrations in these directions are equal to  $f = \kappa c_1/2m$  and  $f = \kappa c_1/2n$ , resonance occurs at rather high frequencies. As  $\kappa_1$  in the expression  $f_x = \kappa_1 c_1/2l$  is given values from 1 to  $\infty$ , a series of resonance frequencies,  $f_d$ , spaced more and more widely apart is obtained. If desired, these frequencies may be converted into the ordinary resonance frequencies which depend on  $(E/\rho)^{1/2}$  by using the relations

$$c_1^2 = \frac{2E(1-\sigma)}{\rho(1+\sigma)(1-2\sigma)} \quad c_2^2 = \frac{E}{2\rho(1+\sigma)}$$

When  $a=\alpha$ ,  $b=\beta$  and  $c=\gamma$ , the same equation,

$$f^2 = f_x^2 + f_y^2 + f_z^2,$$

also holds for waves of distortion, except that  $f_x$  is now equal to  $\kappa_1 c_2/2l$  in place of  $\kappa_1 c_1/2l$ , and therefore smaller than for waves of dilatation. In the more general case,  $\alpha$ ,  $\beta$  and  $\gamma$  form simple ratios with  $a$ ,  $b$  and  $c$ , respectively, so that when, for instance,

$$\alpha = qa \quad \beta = rb \quad \gamma = sc$$

the equation for the frequency becomes,  $c_2$  varying with  $p$ ,

$$\begin{aligned} \frac{p^6}{c_2^6} - \frac{p^4}{c_2^4} (\alpha^2 + \beta^2 + \gamma^2) + \frac{p^2}{c_2^2} (\alpha^2 \beta^2 + \beta^2 \gamma^2 + \alpha^2 \gamma^2 - \frac{\alpha^2 \beta^2}{q^2 r^2} - \frac{\beta^2 \gamma^2}{r^2 s^2} - \frac{\alpha^2 \gamma^2}{q^2 s^2}) \\ - \frac{2\alpha^2 \beta^2 \gamma^2}{q^2 r^2 s^2} - \alpha^2 \beta^2 \gamma^2 \left(1 - \frac{1}{r^2 s^2} - \frac{1}{s^2 q^2} - \frac{1}{q^2 r^2}\right) = 0 \end{aligned}$$

or

$$f^6 - f^4(f_x^2 + f_y^2 + f_z^2) + f^2 \left( f_x^2 f_y^2 + f_y^2 f_z^2 + f_x^2 f_z^2 - \frac{f_x^2 f_y^2}{q^2 r^2} - \frac{f_y^2 f_z^2}{r^2 s^2} - \frac{f_x^2 f_z^2}{q^2 s^2} \right) - 2 \frac{f_x^2 f_y^2 f_z^2}{q^2 r^2 s^2} - f_x^2 f_y^2 f_z^2 \left( 1 - \frac{1}{r^2 s^2} - \frac{1}{s^2 q^2} - \frac{1}{q^2 r^2} \right) = 0.$$

Unless  $a$ ,  $b$  and  $c$  are very large, the equation for  $p$  demands that  $\alpha = a$ ,  $\beta = b$ , and  $\gamma = c$ .

An empirical formula which suffices in the case of longitudinal waves is obtained by replacing the resonance frequencies  $f_x/q$ ,  $f_y/r$  and  $f_z/s$  by  $\mu f$ . The equation then becomes:

$$f^6 - f^4(f_x^2 + f_y^2 + f_z^2) \frac{(1-\mu)}{(1-2\mu)(1+\mu)} + f^2 \frac{f_x^2 f_y^2 + f_y^2 f_z^2 + f_x^2 f_z^2}{(1-2\mu)(1+\mu)^2} - \frac{f_x^2 f_y^2 f_z^2}{(1-2\mu)(1+\mu)^2} = 0,$$

or

$$\frac{(f_x^2 - f^2)(f_y^2 - f^2)(f_z^2 - f^2)}{f^6} - \mu^2 \frac{(f_x^2 + f_y^2 + f_z^2 - 3f^2)}{f^2} + 2\mu^3 = 0.$$

The correct value of  $\mu$  is found by measuring a few overtones and plotting the first term of the equation as a function of  $(f_x^2 + f_y^2 + f_z^2 - 3f^2)/f^2$ . The slope of the straight line obtained for different values of  $kf_x$  and for different rods is equal to  $\mu^2$ , and its intersection with the axes of co-ordinates lies at a distance of  $2\mu$  from the origin. Resonance frequencies obtained with rods of nickel 100 mm. in length, 10 mm. or less in width and height, are in good agreement with this formula (2). As the frequencies of successive overtones of  $f_x$  are introduced, the resonance frequencies of the first series crowd closer and closer together so as to remain below  $f_y$  or  $f_z$ , those in the second and third series spread farther and farther apart, the frequencies in the second series falling between  $f_y$  and  $f_z$ , those in the third series starting above the higher of these two frequencies.

Finally, for the complete wave involving both dilatation and distortion the formulas show that for any group of three values  $f_x$ ,  $f_y$  and  $f_z$  (the resonance frequencies in pure shear) three resonance frequencies are possible. In practical cases only one solution is real, however. (Table 1.)

TABLE I  
SOLUTION OF THE FREQUENCY EQUATION FOR PRISMATIC RODS

$$\left(\frac{f}{F}\right)^6 - 2\left(\frac{f}{F}\right)^4 \frac{2-3\sigma}{1-2\sigma} + \left(\frac{f}{F}\right)^2 \frac{5-6\sigma}{1-2\sigma} - \frac{2(1-\sigma)}{1-2\sigma} = 0$$

$$F^2 = f_x^2 + f_y^2 + f_z^2$$

$\sigma = 0.25$	0.30	0.35	0.40	0.45
$\frac{f}{F} = 2.44$	2.73	3.21	3.76	4.48

In the more general case involving  $a$ ,  $b$ ,  $c$  in addition to  $\alpha$ ,  $\beta$  and  $\gamma$ , the following equation is obtained as the most important practical equation for ordinary longitudinal motion when  $a$ ,  $b$  and  $c$  vanish

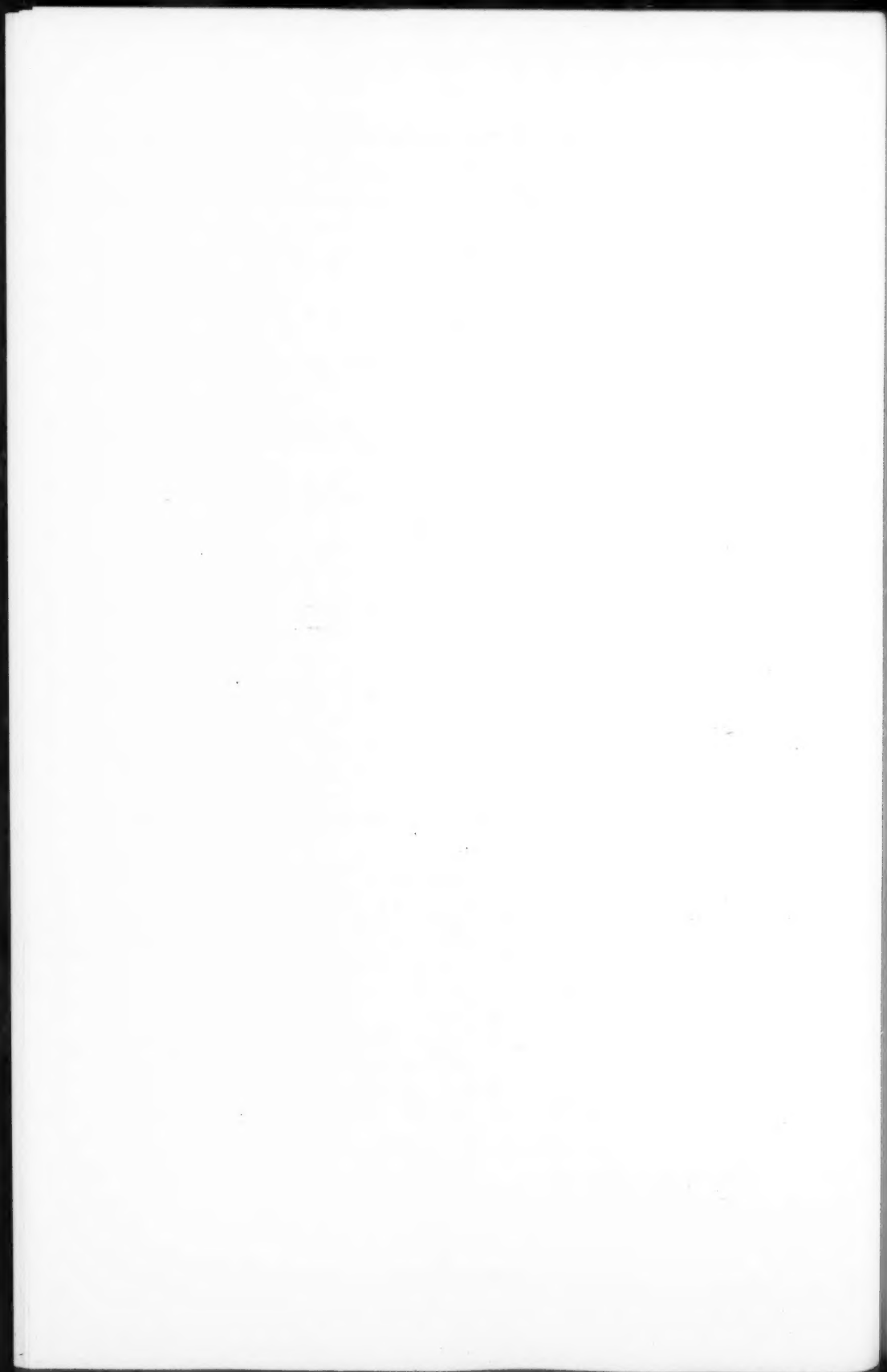
$$f^6 - f^4 \frac{(1-\sigma)}{(1+\sigma)(1-2\sigma)} (f_1^2 + f_2^2 + f_3^2) + f^2 \left( \frac{1-\sigma}{(1+\sigma)(1-2\sigma)} \right)^2 (f_1^2 f_2^2 + f_2^2 f_3^2 + f_1^2 f_3^2) - \left( \frac{1-\sigma}{(1+\sigma)(1-2\sigma)} \right)^3 f_1^2 f_2^2 f_3^2 = 0,$$

where  $f_1$ ,  $f_2$  and  $f_3$  are the ordinary longitudinal resonance frequencies of the rod. A more detailed discussion will be given in a subsequent paper.

The theory thus predicts that a large number of frequencies belonging to different series appear in the range above one of the lateral resonance frequencies of the rod. This is confirmed by experiment.

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# Canadian Journal of Research

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## THE BACTERIAL REDUCTION OF SULPHATES<sup>1</sup>

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### Abstract

The presence of sulphate-reducing bacteria in waters of the Coutts area, as indicated by chemical analyses, has been proved, and they have been shown to be absent from deep wells of the Turner Valley area. A limited number of tests indicates that they are absent from deep wells in the Wainwright area. They have been found in Idaho soils and in sewage.

A procedure for proving their presence is described; pure cultures have been prepared, and some of their biochemical characteristics have been noted.

The significance of the presence of these organisms in deep wells, soils and sewage is discussed, and some problems for further study are indicated.

The formation of hydrogen sulphide by the action of living organisms on sulphates has been demonstrated on various occasions. This utilization of organically combined carbon to form a carbonate from a sulphate with production of hydrogen sulphide may be very important in geochemical and allied studies. Iron-bearing waters may deposit ferrous sulphide, gypsum deposits may be converted to calcite, "sour" soils may become alkaline, and hydrogen sulphide set free in oil field waters may raise the sulphur content of the oil.

In this paper the writer proposes to review briefly previous work on the problem, to give the results of tests on a series of samples, and to present a description of a useful technique for isolation of the organisms.

Early studies indicated that some of the algae, notably *Beggiatoa*, *Oscillaria*, and *Ulothrix*, were capable of forming sulphides from calcium sulphate. Hydrogen sulphide production in stagnant waters is very common, but frequently occurs without a corresponding decrease in sulphate concentration. The writer has made tests (unpublished) which indicate that such sulphate reduction as occurs is indirect: that the sulphate combines with a protein molecule in an animal organism, and hydrogen sulphide is formed later in the bacterial decomposition of the protein. The hydrogen sulphide production may be due to the action of any of several species of bacteria, or to that of algae. It has been ascertained so far that direct sulphate reduction takes place only by bacterial action, and the possible species so far isolated are limited.

The first studies of bacterial reduction of sulphates were those of Zelinsky (12) and Beijerinck (2). Zelinsky studied bacteria isolated from the bottom ooze

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of the Black Sea, and pointed out that the dark color of iron sulphide was due to sulphate reduction. Some of Zelinsky's work has been criticized by Elion (3). Beijerinck isolated his organisms and defined the nature of the reactions taking place. Van Delden (10), Rank (8) and Von Wolzogen (11) isolated sulphate-reducing bacteria from vegetable mold, sea sand and clay, respectively. Elion (4) isolated a thermophilic strain from ditch water. Bastin, Gahl, and Anderson (1, 5, 6) have investigated sulphate-reducing bacteria in oil-field waters, and have pointed out the geological and economic importance of their occurrence.

The only worker to isolate the responsible organism in pure culture was Van Delden (10).

Our present knowledge of the bacterial reduction of sulphates is briefly outlined. Such reduction is in all cases due to an organism of the *Vibrio* group, and occurs only under strictly anaerobic conditions. The chemical reaction is summarized as follows:



where R represents a metal, and C, organically combined carbon. The net result, in water, is an increase in alkalinity, or a replacement of a strong, by a weak, acid.

Three very similar species of bacteria have been described: *Microspira desulphuricans*, a fresh water type; *Microspira aesturii*, a salt water form; and *Vibrio thermodesulphuricans*, a thermophile. Gahl and Anderson (5) consider that all three represent variants of one species.

### Scope of the Present Study

The studies reported in this paper were begun in collaboration with Mr. W. P. Campbell, then chemist to the Department of the Interior, Calgary, who noted that certain oil-field waters in the Coutts area showed abnormally low sulphate concentrations and correspondingly larger amounts of carbonate and hydrogen sulphide. A study of the oil-field waters of Alberta was begun, and further samples were obtained from Dr. T. A. Link and Mr. P. D. Moore, geologists of Royalite Oils Company, Turner Valley. A series of samples of soils and clays from the Kootenay Flats, Idaho, were obtained through the co-operation of Mr. P. A. Fetterley, Dominion Water Power and Reclamation Service, and studies were made of Calgary sewage. In all, about 50 samples were tested.

A technique was developed for isolation of the organisms in pure culture, and tests were made on the organisms so isolated.

### Results of Tests on Samples by Groups

*Group 1.* Turner Valley; 17 samples examined. Sixteen samples, all from depths of more than 1000 ft., showed high concentrations of hydrogen sulphide, occasionally very saline waters. No sulphate-reducing bacteria were isolated in 98 tests. One sample, Vanberta No. 2, obtained at a depth

of 40 ft., a typical surface water, yielded a very weak strain of sulphate-reducing *Vibrio* organisms. This strain did not survive purification, and only preliminary tests were made.

*Group 2.* Wainwright area; 4 samples examined. All gave negative results.

*Group 3.* Coutts area; 4 samples examined. Two gave positive results, and Gram-negative sulphate-reducing *Vibrios* were isolated in pure culture.

*Group 4.* Soils and clays, Kootenay Flats, Idaho. Eight samples were examined; six gave positive results and Gram-negative sulphate-reducing *Vibrios* were isolated in pure culture.

*Group 5.* Calgary sewage; 20 samples examined. Two gave positive results, and extremely active Gram-negative sulphate-reducing *Vibrios* were isolated in pure culture. These positive results were obtained in the presence of packing house waste, and it appears that such material may contain large numbers of sulphate-reducing bacteria.

### Technique and Results of Tests

In all positive tests reported above, the samples were taken in sterilized bottles, using the usual precautions against contamination. With some of the samples giving negative results such refinement could not be observed. Considering the anaerobic nature of the organisms, accidental contamination seems unlikely.

The medium found most satisfactory, and the one finally adopted, is a slight modification of Bastin's 1.1 (1). It consists of: dipotassium hydrogen phosphate, 0.5 gm.; asparagin, 1.0 gm.; magnesium sulphate crystals, 2.5 gm.; sodium lactate, 5.0 gm.; ferrous ammonium sulphate, 0.2 gm.; distilled water, 1 litre; 0.1N sodium hydroxide, 3.5 ml.

The medium may be modified by the addition of sodium chloride or agar (30 gm.) or both. The material is dissolved by boiling, and sterilized in test tubes (25 ml. per tube) under pressure. The final reaction varies from pH 7.0 to 8.0. A slight gray precipitate forms on sterilizing.

The sample is first cultured in the liquid media, with and without sodium chloride (20 gm. per litre). The medium is heated to 100° C. to expel air, and then cooled to 40° C. After inoculation with measured portions of the sample (10 cc. and 1 cc. in the case of a liquid, and 5 gm. and 0.5 gm. in the case of soil), the tops are sealed with sterile, melted "vaseline" to a depth of about 1 cm. The sample is incubated at 37° C. and observed for two to four weeks. At the end of such time the tubes which show progressive darkening of the liquid or sediment, with or without gas formation and softening of the seal, are opened. A second culture is inoculated with a small amount, and the observations are repeated. If similar darkening occurs in the second tube it is considered that the presence of sulphate-reducing organisms is proved. Stained mounts and hanging drop preparations of the liquid medium are examined, and the solid medium may be inoculated with these in order to isolate the organism in pure culture.



The formation of ferrous sulphide in the first tube is not definite evidence of sulphate reduction, since hydrogen sulphide present in the sample will cause this precipitation. The writer did not find the method of pumping off hydrogen sulphide under vacuum, as described by Bastin (1), applicable to the samples tested, and the use of a secondary inoculation was added to routine procedure.

For the purpose of a practical test, the formation of ferrous sulphide over a period of two days to one month in the second tube is regarded as evidence of the bacterial reduction of sulphates, and the presence of motile Gram-negative *Vibrios* in the hanging drop and stained mounts may be considered as a confirmation of the results.

More extensive studies, including purification of the cultures so obtained, are frequently liable to yield inconclusive results, and are therefore not recommended for routine procedure. Such purification is difficult, rather time-consuming, and requires special apparatus. After a series of preliminary tests the equipment shown in Fig. 1 was built.

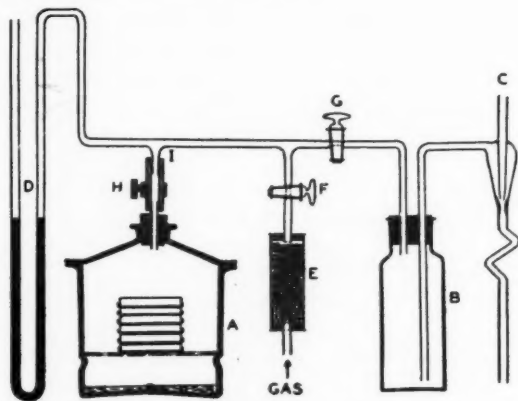


FIG. 1. Anaerobic culture apparatus (not to scale).

A is a vacuum desiccator, the bottom of which is divided into halves by means of a small ridge of modelling clay. On one half is placed a concentrated solution of potassium hydroxide, and on the other a solution of pyrogalllic acid. The Petri dishes containing inoculated media are, as soon as possible after the medium solidifies, inverted in the apparatus, and the cover is sealed on with stopcock lubricant. Stopcock F is closed and G opened, and the aspirator pump C operated until the system is exhausted as completely as possible, as shown by manometer D. The usual pressure is about 50 mm. (Bottle B serves as a safety jar to prevent water being drawn into the apparatus.) Stopcock G is closed and stopcock F opened to admit natural gas purified with soda lime in E. When the pressure has risen to atmospheric, topcock F is closed. The operations of evacuation and filling with gas are

repeated four times. Finally, the pressure in *A* is about 100 mm. less than atmospheric. Screw clamp *H* is then closed and the apparatus disconnected at *I*. The desiccator is tilted slightly to mix the alkali and pyrogallic acid, the pyrogallate so formed absorbing the last traces of oxygen.

The medium previously described, modified by the addition of 30 gm. of agar, gives satisfactory colonies with incubation times of 8 to 12 days. The liquid medium is inoculated with these colonies and it then serves as stock culture for further study.

In general, two definite types were formed on these plates. Type 1, Fig. 2, was obtained from all cultures from samples in Groups 3 and 5. Type 2,

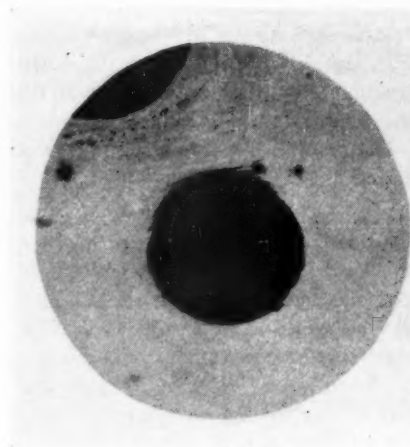


FIG. 2. Colony Type 1.  $\times 50$ .

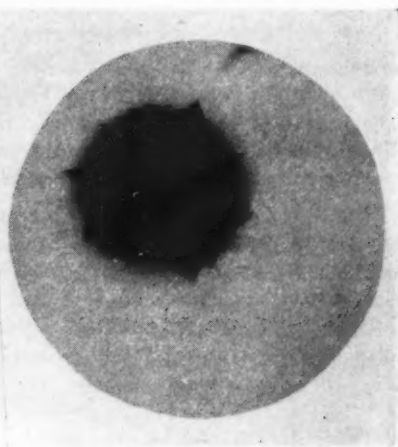


FIG. 3. Colony Type 2.  $\times 50$ .

shown in Fig. 3, was obtained from the clay samples in Group 4. Biochemically and morphologically these are identical, showing the following characteristics:

Small motile *Vibrios*, Gram-negative, with polar flagella; grow in absence or presence of salt in concentrations as high as 3%; strictly anaerobic; when first isolated usually produce sufficient gas to lift the vaseline seals, but lose this activity on continued cultivation; can use lactate but not formate as a source of carbon; increase the alkalinity of culture during growth.

A series of tests was made to determine the optimum pH for good growth. The results of four series of tests on typical strains are shown in Table I.

TABLE I  
EFFECT OF pH ON BACTERIAL GROWTH

pH	Result
Less than 3 —	No growth
3 to 10	Growth, best at pH 5 to 9
10 to 12	Poor growth
12 or higher	No growth

From a few of the cultures which produced gas under the seal, gas samples were collected and analyzed by means of a micro gas burette. In all cases the gas was carbon dioxide, and contained only traces of hydrogen sulphide (absorbed by copper sulphate). It is to be expected that the hydrogen sulphide formed would be fixed as sodium and ferrous sulphides. That such was the case was proved by chemical tests on the culture medium.

### Discussion

While the number of species of these bacteria is evidently very limited, they appear to be widely distributed in nature, and are probably responsible for profound changes in the waters of deep wells and in the mineral constituents of soils. Their presence in sewage may be responsible for the production of odors, and may result in abnormal digestion of sludge in disposal plants. Goudey (7) has pointed out that difficulties due to odor and corrosion resulted from sulphate reduction in the Orange County sewage outfall, though the specific bacteria were not isolated. Other studies, notably that of Smith and Thompson (9) on the Lake Washington ship canal, have indicated the importance of the natural reduction of sulphates.

A point that has not been thoroughly studied, in either this or previous researches, is a consideration of the possible forms of carbon that may be assimilated in the bacterial metabolism. In this work formates were found unsuitable, but a few tests indicated that naphthenic hydrocarbons could be utilized by the organisms, and that cellulose was slowly attacked. Further work on the point would be of theoretical and practical value.

### Acknowledgments

The writer wishes to acknowledge his indebtedness to Mr. J. R. Wood, Assistant City Engineer, Calgary, for the opportunity of testing the sewage samples; to Mr. P. A. Fetterley, Dominion Water Power and Reclamation Service, for samples of soil; to Dr. T. A. Link and Mr. P. D. Moore, Royalite Oil Company, for water samples; and particularly to Mr. W. P. Campbell, of the Department of the Interior, under whose direction this work was begun and whose assistance and advice made it possible.

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## STUDIES ON LIGNIN AND RELATED COMPOUNDS

XXI. INSOLUBLE METHANOL LIGNIN<sup>1</sup>BY HERBERT W. MACKINNEY<sup>2</sup> AND HAROLD HIBBERT<sup>3</sup>

## Abstract

When spruce wood meal is extracted with anhydrous methyl alcoholic hydrogen chloride, about 30% of the lignin can be removed in soluble form. The insoluble lignin in the residual wood can be isolated as a fully methylated derivative by a prior complete methylation with dimethyl sulphate followed by hydrolysis with methyl alcoholic hydrogen chloride. The fully methylated insoluble methanol lignin is insoluble in organic solvents.

Demethylation experiments followed by subsequent treatment with methylating and acetylating agents, alone or combined, have established a very close relation between the insoluble and the soluble form. The formation of the insoluble form from the native lignin is accompanied by loss of one hydroxyl group as indicated in the two formulas: soluble methanol lignin,  $C_{42}H_{32}O_6(OCH_3)_6(OH)_4$ , and insoluble methanol lignin (fully methylated),  $C_{42}H_{32}O_6(OCH_3)_9$ . The new evidence obtained indicates that of the five methoxyl groups present in the original native lignin, at least three are phenolic or enolic in character.

## Introduction

Recent contributions from these laboratories describe the extraction of lignin from spruce wood by means of absolute methanol containing a small amount of hydrogen chloride as catalyst (3). Under this treatment some 50% of the wood is dissolved. On pouring the concentrated methanol solution into water, 25–30% of the total lignin originally present in the wood separates out as an amorphous solid, soluble in methanol and dioxane (designated "methanol lignin"). The insoluble lignin fraction remaining in the wood forms the subject of the present investigation.

The formula for methanol lignin has been established previously (2) as  $C_{42}H_{32}O_6(OCH_3)_6(OH)_4$ , while "native lignin" corresponds to  $C_{42}H_{32}O_6(OCH_3)_5(OH)_5$ . Of the five hydroxyl groups in the "building-unit," one can be readily methylated by means of diazomethane and one by means of methyl alcoholic hydrogen chloride.

## Discussion

*Method of Isolating the Insoluble Methanol Lignin*

The residual wood meal left after exhaustive extraction of the soluble methanol lignin was first completely methylated (dimethyl sulphate). The methylated residue was treated repeatedly with absolute methanol containing a small amount of hydrogen chloride at 100° C. for a prolonged period. The methylated carbohydrates passed into solution, the lignin remaining as a

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Contribution from the Division of Industrial and Cellulose Chemistry, Pulp and Paper Research Institute, McGill University, Montreal, Canada, with financial assistance from the Canadian Pulp and Paper Association. This paper was constructed from a thesis presented by H. W. Mackinney, in October, 1935, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

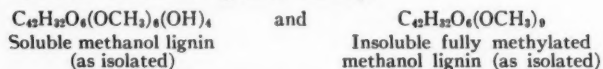
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brown amorphous solid, insoluble in all solvents (designated "insoluble methanol lignin"). The yield of carbohydrate-free product, shown to be fully methylated, was 19% of the original wood used, or approximately 65% of the total lignin contained therein.

Analysis showed: C, 66.6; H, 6.3; O, 27.1;  $\text{OCH}_3$ , 31.2%, as compared with C, 66.2; H, 6.6; O, 27.2;  $\text{OCH}_3$ , 32.4, for fully methylated soluble methanol lignin.

A study of the removal of the methoxyl groups and of their re-introduction by means of methylating agents has indicated a close relation between the soluble and insoluble methanol lignins, namely,



The insoluble methanol lignin differs from the soluble in that the production of the former from native lignin involves the loss of one hydroxyl group per building-unit, presumably resulting in a  $-\text{C}-\text{C}-$  linkage between two lignin molecules.

#### *Demethylation Experiments on Insoluble Methanol Lignin*

The above-mentioned methanol lignin building-unit was first derived from the results of methylation of methanol- and glycol lignins with diazomethane (2), a procedure inapplicable to insoluble methanol lignin unless prior demethylation could be effected.

The literature contains only a few references to demethylation experiments on lignin. Heuser, Schmitt and Gunkel (11) completely demethylated Willstätter lignin using 5% aqueous hydrochloric acid at 170–180° C. Other deep-seated changes occur as shown by analysis and incomplete remethylation. No loss of methoxyl occurred at 160° C., a result contrary to earlier work (10) in which a different Willstätter lignin was used.

Freudenberg, Belz and Niemann (6) studied the rate of removal of methoxyl from lignin and other substances by hydriodic acid ( $d$ , 1.7) at 90° C. They found that whereas aliphatic methoxyl is rapidly removed, methoxyl attached to aromatic nuclei is more resistant. The behavior of lignin was found comparable to that of vanillin, rather than to that of aliphatic substances such as tetramethyl glucose or methyl cellulose. Their demethylated lignin, in contrast with the original lignin, was soluble in alkali, and was precipitated from this solution by means of carbon dioxide. No analyses of the product were reported, nor apparently was any attempt made to remethylate. They concluded that all the methoxyl groups in lignin are similarly (aromatically) combined, and their formula is based largely on this conclusion. It should be pointed out that whereas the reactions between hydriodic acid and vanillin and tetramethyl glucose, respectively, occur in homogeneous solution, that with lignin and methyl cellulose takes place in a heterogeneous system; secondly, their data are insufficient to permit graphic representation. Furthermore, their views do not explain the ease with which methoxyl groups are removed during the halogenation of lignin (6, 7). From their data on the

chlorination of a modified Klason lignin, Harris, Sherrard and Mitchell (9) conclude that the methoxyl groups in lignin are combined in at least three ways: one part readily removable on chlorination with dry chlorine, a second on treatment with aqueous chlorine and a third resistant to chlorination.

Hibbert and co-workers (8) attempted, unsuccessfully, to demethylate glycol lignin, using a mixture of acetic anhydride and acetic acid saturated with hydrogen bromide, but the only reaction was a partial replacement of methoxyl by acetyl. Beckmann, Liesche and Lehmann (1) heated an alkali lignin preparation with hydriodic acid in glacial acetic acid solution, and obtained a completely demethylated lignin which contained chemically bound iodine (7-18%).

The method adopted for demethylation of insoluble methanol lignin in the present investigation was based on the work of Irvine and Hynd (13). These authors studied the removal of the methoxyl groups from tetramethyl glucose by hydriodic acid, and found that the reaction proceeded smoothly with hydriodic acid (29-59%) at temperatures varying from 80 to 114° C. The free glucose was recovered in good yield.

For the writers' demethylation experiments on insoluble methanol lignin a uniform temperature of 100° C. was adopted. Two series of experiments were carried out with hydriodic acid of 50 and 40% concentration respectively. As in its later stages the reaction becomes extremely slow, the demethylation was not usually carried to completion, but interrupted after the methoxyl content had fallen below that equivalent to one methoxyl group (4.6%), the rate of demethylation being then constant.

The change in methoxyl value was determined using three concentrations of hydriodic acid (59, 50, 40%), the methyl iodide formed after definite time intervals being estimated iodometrically (5) (Table I and Fig. 1).

The free hydroxyl groups in the demethylated lignin were determined by re-methylation and acetylation. In the former, diazomethane followed by dimethyl sulphate was employed. With diazomethane an increase in methoxyl to 15.5% occurred, corresponding to four methoxyl groups, while the action of dimethyl sulphate increased this value to 18.5%, equivalent to five methoxyl groups. Acetylation values confirmed these findings, the methylation and acetylation being complete in each case.

That a secondary change had taken place was shown by elementary analysis of the various derivatives which indicated that a condensation had occurred simultaneously with the demethylation. This involved the loss of two molecules of water from four hydroxyl groups with formation of two linkages of an ether type. Such a compound would have the formula  $C_{42}H_{32}O_6(OH)_6 >O>O$ , although, since the demethylation was not carried to completion, the formula  $C_{42}H_{32}O_6(OCH_3)(OH)_4 >O>O$  more nearly expresses the final product. On methylation with diazomethane, the number of methoxyls is increased to four, indicating that these are of an acidic type, either enolic or phenolic. Using dimethyl sulphate, the remaining hydroxyl group was methylated. The analytical results obtained agree well with this interpretation. Similar values were obtained irrespective of whether 50% or 40%



TABLE I

LOSS OF METHOXYL FROM INSOLUBLE METHANOL LIGNIN WITH HYDRIODIC ACID AT 100° C.

Time, hr.	Concentration of hydriodic acid used					
	59%	50%	40%	59%	50%	40%
	Methyl iodide liberated during each interval, as % methoxyl			Methoxyl remaining in lignin, % calculated from loss of OCH <sub>3</sub>		
0.5	—	—	6.7	—	—	24.1
1.0	27.0	15.7	7.7	3.8	15.1	16.4
1.5	—	—	3.0	—	—	13.4
2.0	2.4	5.8	—	1.4	9.3	—
3.0	0.6	1.2	—	0.8	8.1	—
4.0	—	0.8	—	—	7.3	—
4.2	—	—	4.0	—	—	9.4
5.0	—	0.7	—	—	6.6	—
7.0	—	1.3	—	—	5.3	—
7.5	—	—	4.5	—	—	4.9
13.5	—	—	3.5	—	—	1.4
24.5	—	—	2.6	—	—	— 1.2
Methoxyl in isolated demethylated lignin:				—	4.6	0.7
Total methoxyl accounted for:				—	30.1	32.7

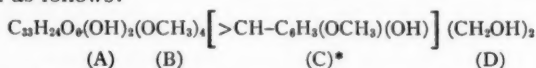
NOTE.—The insoluble methanol lignin used contained 30.8% methoxyl.

hydriodic acid was employed, and in all cases the demethylated products were free from iodine (see Table II).

No demethylation experiments have as yet been carried out with soluble methanol lignin. However, the fact that it is possible to interpret the demethylation data obtained with insoluble methanol lignin on the basis of the formula previously proposed for soluble methanol lignin, indicates a simple relation between both products, as shown above.

On account of the secondary changes occurring during demethylation, the present experiments provide only incomplete data on the nature of the hydroxyl and methoxyl groups in the original native lignin. It would seem, however, that of the nine possible hydroxyl groups liberated during demethylation, four are characterized by a marked tendency towards condensation, and disappear during the process. Such behavior is frequently associated with primary hydroxyls attached to aromatic nuclei. Of the remaining five, four appear to be phenolic or enolic in character, in the light of the ease and extent of methylation with diazomethane. It has been shown previously (2) that "native lignin" contains only one free phenolic hydroxyl group, so that the remaining three "acidic" hydroxyls must be present as methoxyl groups.

On the basis of the present and previously published results of investigations of Hibbert and co-workers, the formula for native spruce lignin may be represented as follows:



\*See Tomlinson and Hibbert (16).



TABLE II  
ANALYSIS OF THE METHYLATED AND ACETYLATED DERIVATIVES OF THE DEMETHYLATED INSOLUBLE METHANOL LIGNIN

Derivative	Found using 50% HI				Found using 40% HI				Calcd. values*			
	C %	H %	OCH <sub>3</sub> %	CH <sub>3</sub> CO %	C %	H %	OCH <sub>3</sub> %	CH <sub>3</sub> CO %	C %	H %	OCH <sub>3</sub> %	CH <sub>3</sub> CO %
Demethylated lignin methylated with diazomethane	—	—	15.5	—	—	—	—	—	—	—	15.4	—
Demethylated lignin methylated with diazomethane and dimethyl sulphate	68.8	5.6	18.5	—	—	—	—	—	68.8	5.8	18.9	—
Demethylated lignin methylated with dimethyl sulphate (directly)	—	—	20.0	—	—	—	—	—	—	—	18.9	—
Demethylated lignin acetylated with CH <sub>3</sub> COCl + C <sub>6</sub> H <sub>5</sub> N	—	—	—	—	65.8	5.2	2.9	18.7	65.5	5.1	3.3	18.3
Demethylated lignin acetylated with (CH <sub>3</sub> CO) <sub>2</sub> O + C <sub>6</sub> H <sub>5</sub> N	—	—	—	—	65.5	5.1	—	17.3	65.5	5.1	3.3	18.3

\*Based on the following formula:  $C_{42}H_{32}O_4(OCH_3)(OH)_4-O_7$

Of the two hydroxyl groups (A), one is of a glucosidic type and disappears in the formation of insoluble methanol lignin, while of the four methoxyl groups (B), three are phenolic or enolic in character. Since recent investigations have proved (12) that there are neither open chain ethylenic linkages nor active carbonyl groups in lignin, the complex  $C_{33}H_{24}O_6$  must be regarded as containing a group of heterocyclic oxygen rings. Whether these are of furan, pyrone, flavone, chromone or other type is not yet known, although in the opinion of one of the writers (H.H.) theoretical and other considerations point to the possible presence of a hydro-pyrone ring.

### Experimental

#### (a) ISOLATION OF INSOLUBLE METHANOL LIGNIN

##### (i) Extraction of Methanol Lignin\*

Spruce wood meal (765 gm., pretreated by the method described by Hibbert *et al.* (8)), was heated at 75° C. for six days with 5000 cc. of absolute methanol containing 2% of anhydrous hydrogen chloride. The residual meal was filtered, washed with methanol, dried and again similarly extracted for a further six days. In all, four such extractions were made. Weight of residue,

435 gm., or 57% of the original wood meal.

TABLE III  
ANALYSIS OF SPRUCE WOOD MEAL BEFORE AND AFTER  
EXTRACTION WITH METHANOL-HYDROGEN-CHLORIDE

	Alcohol- benzene extracted spruce wood, %	Residue after extraction with $CH_3OH-HCl$ , %
Lignin (72% $H_2SO_4$ method)	28.9	30.5
Cellulose (Cross and Bevan)	49.8	60.1
Pentosans (Tollens)	11.5	2.9
Methoxyl	4.9	8.0

The individual methanol extracts were concentrated to about 750 cc. and poured into 10,000 cc. of water containing 60 gm. of potassium bicarbonate. The methanol lignin was separated by filtration and dried. Total yield, 69.5 gm., or 9.1% of the original wood meal (See also Table III).

##### (ii) Methylation of the Wood Meal Residue

The residue obtained as described above (100 gm.) was suspended in acetone (500 cc.) and mechanically stirred. Dimethyl sulphate (400 gm.) and sodium hydroxide (254 gm., as a 30% solution) were added simultaneously, drop by drop, in ten portions over a period of five hours, the mixture being maintained slightly alkaline throughout. In the first two additions the temperature was kept at 20° C., in the second two at 35° C., and during the remainder of the process, at the boiling point of the acetone. One hour after completion of the last addition, the acetone was distilled off and recovered for use in a later batch.

The brown insoluble methylated material was filtered off, washed with water until free from sodium hydroxide and sodium sulphate, and immedi-

\*The authors are indebted to Dr. J. Barsha for carrying out this part of the work.

ately subjected to a second methylation. This was carried out in boiling acetone, 100 gm. of dimethyl sulphate and the equivalent amount of alkali being used for each 100 gm. of residue. The material was worked up as before and dried under reduced pressure at 50° C., finally over phosphorus pentoxide. Yield from 286 gm. of dry spruce residue—255 gm. fully methylated product, or 89.1%.

Analysis:—First methylation:  $\text{OCH}_3$ , 35.8%. Second methylation:  $\text{OCH}_3$ , 34.5; lignin, 35.0%.

The lignin content calculated from the yield and the amount of lignin originally present in the residue amounted to 36%, after allowing for the increase in weight due to methylation—indicating that the loss of lignin, if any, during methylation was small.

(iii) *Isolation of Insoluble Methanol Lignin from the Fully Methylated Residue*

The methylated residue (235 gm.) was heated to 100° C. for 72 hr. with 2,500 cc. of absolute methanol containing 50 gm. of anhydrous hydrogen chloride (=2% by volume). The granular reaction product was filtered off, washed with methanol and water, and dried under reduced pressure at 50° C. Yield, 94.7 gm. Found:  $\text{OCH}_3$ , 31.0%.

On re-treatment, 82.5 gm. yielded 76.3 gm. Found:  $\text{OCH}_3$ , 30.9%. No change was found in either yield or methoxyl value on a third treatment.

(iv) *Examination of Insoluble Methanol Lignin, Isolated as Described above, for the Presence of Impurities*

Examination for cellulose by the method of Cross and Bevan showed a residue amounting to 0.03%, this being of a brownish color. As a further test, 3 gm. was allowed to stand for three days with 50 cc. of 72% sulphuric acid at room temperature, the mixture being then diluted with 1,500 cc. water and boiled for 24 hr. The lignin was filtered off and the filtrate exactly neutralized with baryta. The filtrate, after concentration to a small volume, was tested for reducing sugars with Fehling's solution. The results were negative (14).

Distillation with 12% hydrochloric acid by the method of Tollens yielded a liquid which gave no precipitate with phloroglucinol even on prolonged standing, thus indicating the absence of furfural, and therefore of pentosans, in the lignin. A further portion of the same distillate was tested for formaldehyde by the method of Rimini as modified by Schryver (15), with negative results.

(v) *Elementary Analysis*

Found: C, 66.6; H, 6.3;  $\text{OCH}_3$ , 31.1%. Calcd. for  $\text{C}_{22}\text{H}_{22}\text{O}_6(\text{OCH}_3)_9$ : C, 67.0; H, 6.6;  $\text{OCH}_3$ , 30.6%.

(vi) *Remethylation of Insoluble Methanol Lignin as Isolated*

Insoluble methanol lignin (2.15 gm.) was methylated with dimethyl sulphate (15 gm.) and sodium hydroxide (9.5 gm.) at 56° C. in suspension in acetone. Yield, 2.10 gm. Found:  $\text{OCH}_3$ , 31.2%. The increase of 0.1% is within the experimental error of the analytical method. A second methylation did not increase the methoxyl content.

(vii) *Acetylation of Insoluble Methanol Lignin*

Insoluble methanol lignin ( $\text{OCH}_3$ , 31.1%) (1.35 gm.) was shaken with a mixture of 2 cc. of acetic anhydride and 14 cc. of pyridine for 24 hr. The mixture was poured into ice-water, filtered, washed with water, and dried under reduced pressure over sulphuric acid and sodium hydroxide. Yield, 1.3 gm. Found:  $\text{OCH}_3$ , 30.8;  $\text{CH}_3\text{CO}$ , 0.35%. Sum of  $\text{OCH}_3$  and  $\text{OCH}_3$ -equivalent of  $\text{CH}_3\text{CO}$ : 31.0%. The trace of acetyl is thus due to partial replacement of methoxyl.

(b) DEMETHYLATION EXPERIMENTS

(i) *Demethylation of Insoluble Methanol Lignin with Hydriodic Acid*

The standard procedure adopted consisted in heating the material (usually about 2 gm.) with 20 times its weight of hydriodic acid of the required concentration at 100° C. in a slow current of carbon dioxide. The methyl iodide formed was washed with a suspension of red phosphorus in water and absorbed in a solution of bromine in glacial acetic acid containing 10% of potassium acetate. The iodic acid so formed was determined iodometrically by the method of Viebock and Schwappach (5). The results are plotted in Fig. 1.

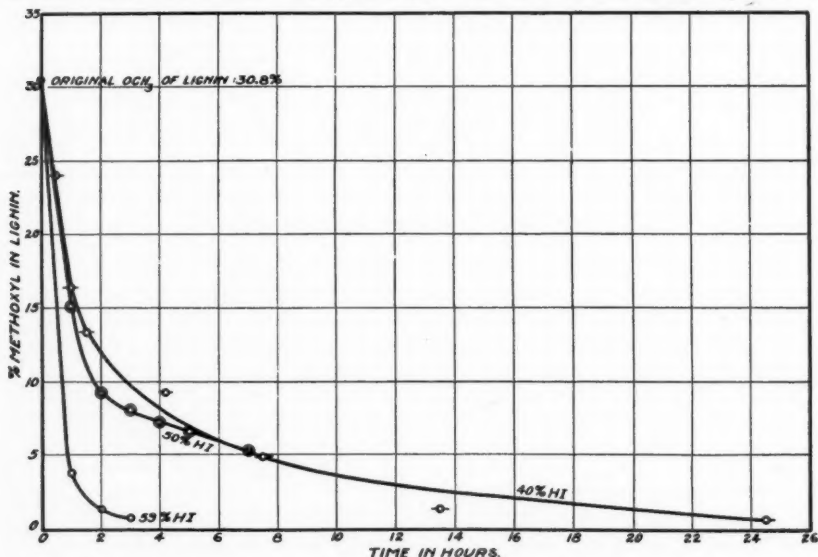


FIG. 1. Removal of methoxyl from insoluble methanol lignin with hydriodic acid.

At the end of the reaction, the mixture was neutralized with sodium bicarbonate solution, the "demethylated" lignin filtered off, washed with aqueous potassium iodide and water, and dried. The dark brown product was free from iodine and insoluble in all organic solvents and in dilute alkali.

*Analysis:* ( $\text{OCH}_3$ )

Series 1, 50% HI: Exp. I, 4.6%; Exp. II, 2.3%.

Series 2, 40% HI: Exp. III, 1.6%; Exp. IV, 4.7%.

Comparison of the acetylated and methylated derivatives indicated that all four had analogous structures.

In the first series, demethylation to 4.5%  $\text{OCH}_3$  (one methoxyl) was complete in 8 hr.; in the second series a longer period was required (about 20 hr.).

(ii) *Methylation of Demethylated Insoluble Methanol Lignin (Preparation I) with Diazomethane*

Demethylated insoluble methanol lignin ( $\text{OCH}_3$ , 4.6%) (1.2 gm.) was moistened with a little water, 40 cc. of cyclohexanol added and the mixture submitted to distillation under reduced pressure until the water had been removed and about 15 cc. of pure cyclohexanol collected. The purpose of this treatment was to increase the reactive surface (4). The solution was diluted with one-tenth its volume of anhydrous ether and given three methylations with diazomethane. After each methylation a sample was taken, filtered, washed with methanol, acetone, ether, benzene, dioxane, petroleum ether, then boiled for 15 min. with water, and dried under reduced pressure over phosphorus pentoxide. Final yield: 1.17 gm. Found:— $\text{OCH}_3$ : First methylation, 13.5; second methylation, 15.4; third methylation, 15.5%. Calcd. for  $\text{C}_{42}\text{H}_{32}\text{O}_6(\text{OCH}_3)_4(\text{OH})-\text{O}_2-$ :  $\text{OCH}_3$ , 15.4%. The reddish-brown amorphous product was insoluble in all solvents.

(iii) *Complete Methylation of the Diazomethane-methylated Product*

The product (0.3 gm.) described in the preceding paragraph was suspended in a mixture of 5 cc. of pyridine and 2 cc. of acetic anhydride at room temperature for 48 hr. The reaction product was poured into ice-water, filtered, washed with water and air-dried. It was suspended in 5 cc. of acetone and methylated at 25–30° C. by simultaneous addition of 6 cc. of dimethyl sulphate and 7 cc. of 7.5 N NaOH. Found:— $\text{OCH}_3$ : First methylation, 18.2; second methylation, 18.5%. After second methylation, C: 68.8, H, 5.6%. Calcd. for  $\text{C}_{42}\text{H}_{32}\text{O}_6(\text{OCH}_3)_6-\text{O}_2-$ : C, 68.8; H, 5.8;  $\text{OCH}_3$ , 18.9%. The methylated product was a reddish-brown amorphous powder insoluble in all solvents.

(iv) *Treatment of the Diazomethane-methylated Lignin with p-Toluene-sulphonyl Chloride at Room Temperature*

Diazomethane-methylated lignin (0.58 gm.;  $\text{OCH}_3$ , 15.5%), obtained as described above, was suspended in a solution of 2 gm. of *p*-toluene-sulphonyl chloride in 5 cc. of pyridine. The mixture was shaken at room temperature

for eight hours, allowed to stand for 40 hr. and poured into ice-water. The tosyl ester was isolated as a dark brown powder, insoluble in all solvents. Yield, 0.68 gm. Found:  $\text{OCH}_3$ , 12.3; S, 3.8%. Calcd. for  $\text{C}_{42}\text{H}_{32}\text{O}_6(\text{OCH}_3)_4-(\text{C}_7\text{H}_7\text{SO}_3)-\text{O}_2-$ :  $\text{OCH}_3$ , 12.9; S, 3.3%.

(v) *Acetylation of Demethylated Insoluble Lignin (Prep. IV)*

Demethylated insoluble methanol lignin (0.5 gm.) was allowed to stand for 24 hr. with 10 cc. of pyridine and 5 cc. of acetic anhydride at room temperature. The product was isolated in the usual manner. Yield, 0.55 gm. Found: C, 65.5; H, 5.0;  $\text{CH}_3\text{CO}$ , 17.3%. Calcd. for  $\text{C}_{42}\text{H}_{32}\text{O}_6(\text{OCH}_3)-(\text{CH}_3\text{CO})_4-\text{O}_2-$ : C, 65.5; H, 5.1;  $\text{CH}_3\text{CO}$ , 18.3;  $\text{OCH}_3$ , 3.3%.

(vi) *Acetylation of Demethylated Lignin (Prep. IV), Second Method*

Demethylated lignin (1.0 gm.) was acetylated with 10 cc. of pyridine and 5 cc. of acetyl chloride, considerable heat being evolved. Yield, 1.7 gm. Found: C, 65.8; H, 5.2;  $\text{CH}_3\text{CO}$ , 18.7;  $\text{OCH}_3$ , 2.9%.

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## AN INVESTIGATION OF THE ACTION OF CARBON DISULPHIDE AND AQUEOUS POTASSIUM HYDROXIDE SOLUTIONS ON ALKALI LIGNIN<sup>1</sup>

BY R. L. GLOVER<sup>2</sup> AND J. W. BAIN<sup>3</sup>

### Abstract

Carbon disulphide and aqueous potassium hydroxide solutions act on alkali lignin, forming very viscous mixtures from which colloidal, lignin-like materials containing sulphur and of high molecular weight may be isolated.

The hypothesis is advanced that a lignin xanthate may be a step in a theoretical series of reactions culminating in the formation of the materials isolated.

The presence and condition of the sulphur in the isolated product are discussed from the standpoint of this hypothesis.

In December, 1933, a color reaction was observed in this laboratory which led to the belief that carbon disulphide reacts with alkali lignin. A careful examination of the literature available failed to reveal any knowledge of such a reaction. Mehta (7) states that ligno-cellulose does not take part in the cellulose xanthate reaction. An investigation was accordingly begun, but progress was slow, owing to difficulties in the separation and isolation of the products. While endeavoring by various means to obtain larger amounts of the products, the very striking change in the viscosity of the reaction mixture which will be fully described below, was discovered.

Before describing the experimental work, the reactions of the xanthates will be briefly reviewed. The xanthate reaction has long been known as a general reaction of alcohols. Formation of xanthic acid salts by the reaction of carbon disulphide and alkali takes place not only with simple alcohols, but with other compounds, such as hydroxy acids and cellulose, having alcoholic hydroxyl groups. The reaction has been used extensively in the investigation of the terpene alcohols; and while the esters of the xanthic acids of the primary and secondary alcohols of this series may be easily isolated, those of the tertiary alcohols decompose, forming the corresponding unsaturated hydrocarbons (4). This is an indication that the xanthates of tertiary alcohols are more unstable than those of the primary and secondary alcohols. Xanthates in general are quite unstable when heated in the presence of water; above 50° C. they slowly decompose, forming various products such as carbon disulphide, potassium hydroxide, thiocarbonate and mercaptans.

Some of the properties of the more complicated xanthates are very interesting in the light of work on lignin. Cross, Bevan and Beadle (3, p. 248) precipitated cellulose xanthate by coagulation, using a solution of strong alcohol or saturated brine. "Coagulation of the cellulose product proceeds

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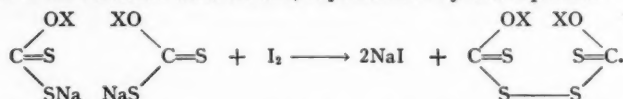


gradually, and after some time a coherent slab is obtained of greenish colour, the yellow by-products of the reaction being dissolved by the alcohol." After the xanthate, purified either by salting out or by coagulation with alcohol, had been redissolved and reprecipitated several times, it showed a progressive diminution in alkali and sulphur content on the basis of the cellulose, while the ratio of alkali to sulphur remained constant. Later the same authors (3, p. 338) established the fact that cellulose xanthic acid was considerably stronger than acetic acid and monocarboxylic acids in general. Hence, if solutions of the crude compound were treated with acetic acid, the by-products were decomposed and the alkali salt of cellulose xanthic acid was not affected. It could be precipitated with alcohol, and the isolation of pure compounds of the series was much facilitated. The general formula



was verified with satisfactory precision; X was a cellulose residue of various dimensions. When the compound was freshly prepared, X lay between a  $\text{C}_8$  and  $\text{C}_{12}$  complex, and the compound was not precipitated by dehydrating agents; as X approached a  $\text{C}_{12}$  complex, the xanthate was precipitated by alcohol, and redissolved in water; as X approached a  $\text{C}_{24}$  complex the xanthate was precipitated by alcohol solution, was completely precipitated by acetic acid, and thus was insoluble in water.

Another reaction of cellulose xanthate which may be used for its quantitative estimation is its reaction with iodine, represented by the equation



With this account of the properties of xanthates for comparison, the action of carbon disulphide and caustic potash on lignin will now be described.

#### The Action of Carbon Disulphide and Potassium Hydroxide Solutions on Alkali Lignin

Alkali lignin was prepared by the method of Mehta (7). White spruce (*Picea canadensis*) was ground to pass a 40 mesh screen, extracted with a 1 : 1 mixture of benzene and ethyl alcohol, and then with a cold 5% solution of sodium hydroxide to remove resins, fats, tannins and hemicelluloses. The crude lignin, after precipitation from the black liquor, was used in the reaction mixtures, as it was discovered that the action was the same as that with highly purified forms of lignin. The lignin, an analysis of which is given in Table II, was further purified by dissolving it in hot nitrobenzene, filtering the solution, and allowing it to cool. The lignin which separated out was filtered off, washed thoroughly with benzene and dried. The formula corresponded to  $\text{C}_{21}\text{H}_{22}\text{O}_4$ . This was established as the molecular formula by the freezing point method, using phenol as the solvent. Mol. wt.—Calcd. 370. Found, 367.

When aqueous solutions containing 10 to 15% of alkali lignin and 10 to 15% of potassium hydroxide were shaken with carbon disulphide for 8 to 16 days in a glass stoppered bottle at room temperature, an interesting series of phenomena was observed. The lignin formed a clear, very dark brown solution with the potassium hydroxide and water; this floated on the carbon disulphide. When the aqueous layer and carbon disulphide had been in contact for less than two or three days, and the bottle was then shaken vigorously, the carbon disulphide broke up into small globules distributed throughout the aqueous layer; these immediately coalesced to form a clear layer again when shaking was stopped. There were no signs of emulsification. However, when the two layers had been in contact for several days, the aqueous layer became noticeably more viscous, and on shaking vigorously as before, the carbon disulphide dispersed more fully and took longer to coalesce. The aqueous layer gradually became more viscous till it was quite jelly-like, after a period varying from 8 to 15 days. If continually shaken for this length of time, the product was almost solid, containing emulsified carbon disulphide. When the shaking was discontinued after the aqueous layer showed signs of becoming viscous, the carbon disulphide settled out slowly, and the aqueous layer became more and more viscous till it set as a clear, dark-brown jelly (A), with a layer of emulsified carbon disulphide underneath. Further standing caused (A) to become opaque, and a thin, red-brown liquid, containing no lignin, separated from a pasty mass of material. As long as (A) remained a clear, dark jelly, it was soluble in water, but when the reaction continued the pasty mass that formed was insoluble.

A blank mixture, similar in composition to the reaction mixture, but containing no lignin, gave no signs of increasing viscosity after it had been shaken for several weeks; neither was any emulsion formed.

This definite change in viscosity, even though the mixture was not shaken after the change had started, indicated that a reaction had taken place. There were two possibilities: (i) the phenomenon may have been purely physical and the increase in viscosity due to the formation of an emulsion of the carbon disulphide and the aqueous liquor; (ii) a chemical reaction may have taken place, the viscous nature of the reaction product making emulsification of the carbon disulphide possible. The formation of such viscous solutions in water is a property peculiar to xanthates of starch and cellulose.

A reaction mixture was shaken till the whole became solid and was then allowed to stand until a small amount of thin, red-brown liquid separated from the resulting pasty mass. Examination of a drop of this material under the microscope revealed a certain amount of carbon disulphide suspended as droplets in a mass that had no definite structure. Vague outlines of very attenuated brown solid particles were observed. The addition of a drop of water revealed that there was a highly dispersed, difficultly soluble solid present. Moreover, the droplets of carbon disulphide differed a great deal in size. This is unlike the disperse phase of an emulsion. These facts support

the view that the phenomenon has a chemical, and not merely a physical, cause. The increase of viscosity was repeatedly observed; it occurred without exception.

When the concentration of the lignin was 5% or less, a brown, highly dispersed solid separated out of the solution, and the liquid did not become noticeably more viscous till this took place.

This change in viscosity of the solutions was followed by means of an Ostwald type viscometer.

TABLE I  
VARIATION OF VISCOSITY OF REACTION PRODUCTS WITH TIME

A		B		C	
T, days	t, sec.	T, days	t, sec.	T, days	t, sec.
0	8	0	8.4	0	6.8
9	125	1	8.2	1	6.8
10	$\infty$	2	8.0	2	6.8
		3	7.8	3	6.8
		5	8.2	5	6.8
		6	8.8	6	6.4
		7	42.2	7	6.2
		8	Pasty	8	6.0

NOTE: *T* is the time during which the reaction mixture was shaken.

*t* is the time required for the aqueous product to pass two marks on the capillary tube of the Ostwald type viscometer.

*A* is the clear, dark, aqueous liquid layer of a reaction mixture of 6.5 gm. of potassium hydroxide, 5 gm. of lignin, 50 cc. of water, with 15 cc. of carbon disulphide.

*B* is the aqueous layer of 20 gm. of lignin and 60 gm. of potassium hydroxide in 500 cc. of water with excess carbon disulphide.

*C* is the aqueous layer of a blank mixture of 60 gm. of potassium hydroxide, and 500 cc. of water with excess carbon disulphide.

From *B*, Table I, it is evident that there was a sudden rise in viscosity after a number of days. This was always observed with dilute lignin solutions. With stronger lignin solutions, such as *A*, there was a more gradual change in viscosity, although during the last day the viscosity increased enormously. In the latter case it was possible to obtain a clear, dark, viscous, aqueous layer, whereas in the former, a finely divided suspended material precipitated out.

#### Isolation and Analysis of the Reaction Product

The problem of the isolation and purification of the reaction product was quite different from that presented by cellulose xanthate. It was discovered that acetic acid decomposed any xanthate of lignin, if such were formed, as well as the thiocarbonate by-products. For this reason Cross and Bevan's (3, p. 338) method of analyzing for alkali, bound as xanthate, could not be used. Neither did iodine titrations give values that could be interpreted. Lignin itself has an iodine number, and potassium hydroxide reacts with iodine. Attempts were made to titrate with iodine a lignin solution in potas-

sium hydroxide, a blank mixture of potassium hydroxide and carbon disulphide, and a lignin reaction mixture, all of similar strength, but the results could not be interpreted satisfactorily. For this reason it was deemed necessary to actually isolate the product and analyze it. Lignin itself, owing to its amorphous and colloidal nature, is very difficult to handle, and since xanthates are unstable the isolation must be carried out at low temperature and with materials as inert as possible. Attention naturally turned to the use of alcohols or brine as a precipitating agent. Since the precipitates given by brine were very difficult to filter, alcohol was used.

Many different precipitating liquids were tried before satisfactory conditions of precipitation were attained. These were all checked using a blank reaction mixture to ascertain whether thiocarbonates were precipitated when lignin was absent. Ethyl alcohol was used to precipitate the product of the first reaction mixture; subsequently it was found that potassium thiocarbonate was also precipitated by this liquid from the blank mixture, and this led to erroneous results when the precipitated material was analyzed. The following liquids were tested, using blank reaction mixtures: ethyl alcohol, butyl alcohol, amyl alcohol, ethyl alcohol and ethyl acetate, ethyl alcohol and benzene, ethyl alcohol and ether, methyl alcohol and benzene, and methyl alcohol and ether. All these liquids precipitated potassium thiocarbonate as a red oil from the blank mixture. However, when about 5% of water was added to any of the above mixtures, no precipitation ensued either from a blank or from a lignin reaction mixture.

Several batches of reaction product were precipitated by a mixture of ethyl alcohol and ethyl acetate. With blank reaction mixtures of certain concentration this caused no precipitation. The mixture could not be used in all cases, as the water content of the reaction mixture governed the precipitation of thiocarbonate. Methyl alcohol precipitated nothing from either a blank solution or a reaction mixture; a mixture of seven parts of methyl alcohol with three parts of ethyl alcohol was found to have no effect on any blank mixture, whereas a yellow-brown, flocculent, ligneous material was precipitated immediately from a reaction mixture; this could be readily filtered.

Several batches of reaction product were precipitated with a solution consisting of methyl and ethyl alcohols as described above; from the ultimate analyses of these precipitates it was discovered that considerable oxidation had taken place. For this reason a Buchner funnel was fitted with a glass hood which permitted filtering the precipitated material in a stream of nitrogen.

Material 1, Table II, was prepared as follows: A mixture of the composition indicated in the table, the aqueous layer of which amounted to about 70 cc., was shaken with 20 cc. of carbon disulphide until the viscosity of the aqueous layer began to increase. The bottle was allowed to stand until the liquid became very viscous; 140 cc. of methyl alcohol was then added, the whole forming a clear, dark-brown solution. To this, 60 cc. of ethyl alcohol was added, and immediately a light yellow, flocculent precipitate was thrown out

of a thin, red-brown solution. This precipitate was filtered in a stream of nitrogen on a Buchner funnel with slight suction, washed thoroughly with some of the precipitating mixture, with methyl alcohol alone, and finally with ether, and then dried in a stream of nitrogen. Throughout the whole manipulation, air was excluded so far as possible. In this case the oxidizing action of the air was eliminated, and the oxygen content was not as great as that when the material was filtered exposed to air.

It was suspected that oxidation might take place when a solution of lignin in aqueous potassium hydroxide was allowed to stand for some time. It was determined by experiment that oxygen was absorbed (see Material 2, Table II). This will be discussed later.

Additional reaction products similar to No. 1 were made up, the precipitate being thrown down with the methyl-ethyl alcohol mixture as already described; the resulting filtrate including the wash liquid was allowed to evaporate exposed to air. The dry residue was a mixture of needles of crystalline potassium thiosulphate and a brown, ligneous material that could be extracted with hot methyl alcohol. Potassium thiosulphate was insoluble in this solvent, any thiocarbonate had disappeared during evaporation, and no additional sulphur compound could be identified. After evaporation of the methyl alcohol, the extracted ligneous material was a brown, lignin-like substance having a peculiar odor; it proved on analysis to contain sulphur which must, from the circumstances attending its preparation, be chemically combined with the lignin. Analyses of two different preparations are given as Nos. 3 and 4, Table II.

TABLE II  
ANALYSIS OF PRECIPITATES

Material	Precipitating liquid	Lignin/ H <sub>2</sub> O	KOH/ H <sub>2</sub> O	Time of shaking, days	C %	H %	O %	S %	K %	C/H	K/S
1 Filtered in nitrogen	3 ethyl alcohol 7 methyl alcohol	0.080	0.080	11	57.6	5.03	28.2	1.7	7.5	11.45	4.4
2* Filtered in air	3 ethyl alcohol 7 methyl alcohol	0.091	0.087	30	47.9	4.17	33.7	—	14.2	11.48	—
3 Extracted from residue with CH <sub>3</sub> OH	—	—	—	—	45.8	4.54	31.6	3.16	14.9	10.1	4.7
4 Extracted from residue with CH <sub>3</sub> OH	—	—	—	—	37.2	3.80	35.3	4.07	19.6	9.8	4.8
Lignin	—	—	—	—	68.0	5.95	26.05	—	—	11.42	—

NOTE:—All experiments were conducted at room temperature, approximately 20° C.

\*No. 2 mixture did not contain any carbon disulphide.



### The Formation of Thiosulphate in the Reaction Mixture

Another phase of the work was carried out, following as far as possible the course of reaction. It seemed rather peculiar that thiosulphate should form in large quantities, but this was established soon after work began. A reaction mixture of lignin, potassium hydroxide, water and carbon disulphide was shaken in a stoppered bottle for 13 days. Absolute alcohol was then added, and the precipitate formed was filtered off and washed. From the filtrate there separated three successive crops of material consisting of needle-like crystals and brown, amorphous, lignin-like material. Each succeeding crop contained a larger amount of crystals, the third being virtually pure. These needles were separated and examined; their reactions and analysis indicated potassium thiosulphate. The crystals were ground with cupric oxide and the mixture was strongly heated. The gases driven off did not produce any precipitate in a barium hydroxide solution; thus there was no carbon present.

To investigate the action of lignin in reaction mixtures, a series of experiments was carried out to determine the amount of sulphate, thiocarbonate and thiosulphate present. The results, when reaction mixtures were shaken in closed bottles for some time, are given in Table III. Those obtained when the reaction mixtures were stirred in air are given in Table IV.

In an attempt to discover whether potassium ethyl xanthate had any action

TABLE III

AMOUNTS OF SULPHATE, THIOCARBONATE AND THIOSULPHATE PRESENT (REACTION MIXTURES SHAKEN IN CLOSED BOTTLES)

Mixture*	Grams per 100 cc. of mixture		
	K <sub>2</sub> SO <sub>4</sub>	K <sub>2</sub> CS <sub>2</sub>	K <sub>2</sub> S <sub>2</sub> O <sub>3</sub>
1	0.04	4.9	0.28
2	0.28	11.1	0.44
3	0.11	4.6	0.57
4	0.07	6.3	0.35
5	0.91	11.6	0.28
6	—	—	> 4

\*1-4. Potassium hydroxide solutions shaken with 50 cc. of carbon disulphide for various periods of time. 1. 400 cc. of 12% solution; 28 days. 2, 3 and 4. 500 cc. of 15% solution; 18, 4 and 7 days, respectively.

5. Clear, thin, supernatant liquor (containing no lignin) from a mixture of 500 cc. of 15% potassium hydroxide, 16 gm. of lignin, and 50 cc. of carbon disulphide, shaken 15 days.

6. 15% potassium hydroxide plus 10% of lignin precipitated with alcohol.

TABLE IV

AMOUNTS OF THIOSULPHATE AND THIOCARBONATE PRESENT (REACTION MIXTURES STIRRED WHILE EXPOSED TO THE AIR)

T	Grams K <sub>2</sub> S <sub>2</sub> O <sub>3</sub> per 100 cc. of:		Grams K <sub>2</sub> CS <sub>2</sub> per 100 cc. of:	
	A	B	A	B
1	0.140	0.140	6.1	4.6
3	0.126	0.826	9.7	7.8
5	0.735	1.01	17.2	15.4
7	0.801	1.07	17.7	15.7
10	0.870	1.34	19.3	18.1

T—time of stirring, in days.

A—300 cc. of 15% potassium hydroxide solution stirred with 50 cc. of carbon disulphide while exposed to air.

B—300 cc. of the same 15% potassium hydroxide solution with 14 gm. of lignin added—stirred with 50 cc. of carbon disulphide while exposed to air.

on lignin, it was found that, after allowing a mixture of the two to stand in a stoppered bottle for several weeks with ethyl alcohol, no solution of the lignin was observed, there was no xanthate left, and crystals of potassium thio-sulphate appeared. This may throw light on the formation of thiosulphate.

### Discussion of Results

It was rather difficult to interpret the analytical results for Materials 1 and 2, Table II. It is quite evident that the C/H ratio was not appreciably changed from that of the original lignin, although a certain amount of oxidation took place even in Material 1, despite all precautions. Material 1 was not a xanthate, as the low sulphur content shows. Calculations were made as to what the lignin itself must add on to form the materials obtained.

From the ultimate analyses of Materials 1 and 2, and lignin, from which the calculations in Tables V and VI were made, it is clear that oxidation took place during the preparation of the first two.

While this evidently affected the lignin molecule, it did not necessarily have any connection with the sulphur, as the results with Material 2 indicate. Material 1, precipitated from the reaction mixture with carbon disulphide, contained less potassium than that from potassium hydroxide solution (Material 2) alone.

These results alone throw little light on the situation. It must be noted that the product represented by Material 1 was insoluble in sodium hydroxide solution, even on boiling. Also it was insoluble in aqueous acetone and pyridine, two excellent solvents for alkali lignin. Even after Material 1 had been placed in dilute hydrochloric acid to remove the potassium, these insolubilities were unchanged. Material 2 was considerably different in its properties. It was partially soluble in sodium hydroxide solution, and quite soluble in acetone and pyridine contain-

TABLE V  
MATERIAL 1—TABLE II

	C	H	O	S	K
1	57.6	5.03	28.2	1.7	7.5
1 × 68.0 57.6	68.0	5.94	33.2	2.0	8.8
Lignin	68.0	5.95	26.1	0	0
Added to lignin	0	0	7.1	2.0	8.8
			K	S	O
Gram atoms added to 100 gm. of lignin			0.23	0.06	0.45
Gram atoms added to 4.5 gm. molecules of lignin			3.9	1	7.7

TABLE VI  
MATERIAL 2—TABLE II

	C	H	O	K
2	47.9	4.17	33.73	14.2
2 × 68.0 47.9	68.0	5.92	47.9	20.2
Lignin	68.0	5.95	26.1	0
Added to lignin	0	0	21.8	20.2
			K	O
Gram atoms added to 100 gm. of lignin			0.52	1.4
Gram atoms added to 0.52 gm. molecules of lignin			1	2.7



ing a little water, although in each case there was some insoluble material present. These properties, coupled with the fact that acetic acid precipitated a light yellow, easily filtered material from a reaction mixture containing carbon disulphide, whereas it precipitated a gray-brown, highly dispersed, difficultly filterable material from a solution of lignin in aqueous potassium hydroxide, lead one to believe that polymerization had taken place. Since no solvent could be found for Material 1, no molecular weight determination could be made. The solubility of lignin and similar materials seems to depend on their degree of polymerization.

The role of sulphur in the reaction is obscure, as is its ultimate relation to the lignin molecule. As stated above, it is quite evident that a xanthate was not isolated, but an explanation of the action might easily postulate the formation of a xanthate of a tertiary alcohol group in the lignin molecule, its decomposition into the corresponding unsaturated body, with subsequent polymerization to bodies of different complexity containing sulphur linked in the molecule in a manner indicated below:



R represents an oxidized lignin molecule.

Thus a mixture of substances of different degrees of polymerization might be formed.

From the analysis of Material 1 and the above calculations, it is evident that there was one sulphur atom to every four or five lignin molecules.

The phenolic hydroxyl group present need not be disturbed under these circumstances, and the formation of a potassium salt would still be possible. However, the above mechanism is merely a suggestion which further work on the subject will either corroborate or disprove.

The possibility that this sulphur might be adsorbed has not been overlooked. It cannot be adsorbed as sulphate or in any other highly oxidized form, since when sodium sulphate was destructively distilled with lignin only very slight traces of hydrogen sulphide were detected in the vapors, whereas during the destructive distillation of the Lignin-sulphur Material 1, copious amounts of hydrogen sulphide were detected in the vapors by means of lead acetate paper.

Whether sulphur was present as adsorbed free sulphur or potassium thiocarbonate does not lend itself to such direct proof. Each of these would cause hydrogen sulphide to be evolved if the lignin material containing them was destructively distilled. Attempts were made to detect these materials as follows: A small amount of the Lignin-sulphur Material 1 was boiled five minutes with a solution of 0.5 gm. of sodium hydroxide in 10 cc. of water. The mixture was then diluted to 20 cc., cooled, and a few drops of sodium nitroprusside solution was added. No violet color, such as would be caused by sulphides or thiocarbonates, was developed. A mixture of lignin and sulphur treated in a similar manner showed a sulphide reaction, but when only

a very small amount of sulphur was present no color change could be detected, owing to the masking effect of the lignin color. However, if thiocarbonate were present, since it is quite unstable, it is quite certain that it would decompose, forming products having a disagreeable odor. This was noticed with materials precipitated from reaction mixtures by ethyl alcohol. These were known to contain thiocarbonate, and they had a distinctly disagreeable odor like that of decomposing potassium ethyl xanthate. These materials gave a sulphide reaction when treated as outlined above. Material 1, Table II, was odorless.

The presence of free sulphur in the reaction mixture would be difficult to explain. From the above facts it is considered rather unlikely that the sulphur was present in Material 1 as free sulphur, or potassium thiocarbonate.

The only other possibility is that the sulphur was present as potassium thiosulphate. Table III shows that the amount of potassium thiosulphate present in the reaction mixture is very low compared with that of potassium thiocarbonate. It is unlikely that potassium thiosulphate would be adsorbed

selectively from the reaction mixture when present in such a comparatively small amount.

The only other conclusion possible is that the sulphur was chemically combined with the lignin. The above facts point to this, but definite proof is difficult with non-crystalline solids.

Materials 3 and 4 are no less interesting to discuss, and are treated in a similar manner.

These materials dissolved quite readily in water and also in methyl alcohol; they were evidently not polymerized. Again it is noticed that considerable oxidation took place. The carbon-hydrogen ratio was quite different from that of the original lignin, and unless some of the lignin was decomposed, forming molecules of different complexity, it is quite possible that Materials

TABLE VII  
MATERIAL 3—TABLE II

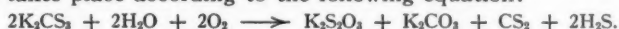
	C	H	O	S	K
3	45.8	4.54	31.6	3.16	14.9
$3 \times \frac{68.0}{45.8}$	68.0	6.74	47.8	4.78	22.1
Lignin	68.0	5.95	26.1	0	0
Added to lignin	0	0.79	21.7	4.8	22.1
		H	K	S	O
Gram atoms added to 100 gm. of lignin		0.79	0.57	0.15	1.3
Gram atoms added to 1.8 gm. molecules of lignin		5.2	3.8	1	8.8

TABLE VIII  
MATERIAL 4—TABLE II

	C	H	O	S	K
4	37.2	3.80	35.3	4.07	19.6
$4 \times \frac{68.0}{37.2}$	68.0	6.94	64.5	7.43	35.7
Lignin	68.0	5.95	26.1	0	0
Added to lignin	0	0.99	38.4	74.3	35.7
		H	K	S	O
Gram atoms added to 100 gm. of lignin		0.99	0.91	0.23	2.4
Gram atoms added to 1.2 gm. molecules of lignin		4.3	4.0	1	10.5

3 and 4, Table II, were formed from some substance present in the crude lignin. It was discovered that the crude lignin could be separated into two distinct fractions by means of a chloroform-ethyl alcohol mixture as solvent. Thus, it is quite possible that these substances (Materials 1 and 4) were formed from some closely related substance present in the original lignin. While the composition of these two materials varies, the presence of sulphur appears to be beyond question; the complexes are probably variable in composition, as is the case with similar sulphur complexes of cellulose and starch.

The formation of potassium thiocarbonate during the reaction is very interesting. It is well known that potassium hydroxide solutions, when shaken with carbon disulphide, form solutions of potassium thiocarbonate, and this may be precipitated as a red oil when alcohol is added. Mellor (8) states that the conversion of potassium thiocarbonate to potassium thiosulphate takes place according to the following equation:



Examination of Tables III and IV indicates that the reaction mixtures contained very little potassium thiosulphate even when stirred while exposed to air. After the addition of the precipitating agent (alcohol), thiosulphate was formed in large quantities, as shown by the results obtained with Mixture 6, Table III. Lignin mixture (B), Table IV, contained roughly 1.5 times the amount of thiosulphate formed in a mixture (A, Table IV) of similar composition containing no lignin.

The complete conversion of some potassium xanthate to potassium thiosulphate, as noted above, may give some clue to the mechanism of the reaction. This suggests that a xanthate was first formed, and that it was subsequently oxidized to thiosulphate.

The xanthates of cellulose and starch are notably unstable. When they are allowed to stand in solution the amount of alkali and sulphur bound in the xanthate becomes less as time proceeds. Lieser (5, 6) notes two important facts; acetic acid decomposes xanthates, though not nearly so rapidly as it decomposes thiocarbonates, and in some cases xanthates decompose on standing with normal sodium hydroxide solution. Atsuki (1, 2) discussed various physical properties of viscose solutions and concluded that the viscose was at first very much hydrated. Ripening consisted of dehydration of particles, followed by coagulation. The latter phenomenon parallels that observed with lignin reaction mixtures.

At the present time it is difficult to offer more than the above observations, and the conclusions they suggest.

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